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PROCEEDINGS OF SYMPOSIUM ON 1975 NORTHEAST OXIDANT TRANSPORT STUDY

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Research Triangle Park, North Carolina
January 20-21, 1976

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The preliminary results of the 1975 Northeast Oxidant Transport Study were presented by the participants of the study at a symposium held at the Environmental Research Center in Research Triangle Park, NC, on January 20-21, 1976. The participants included the Environmental Protection Agency's Environmental Sciences Research Laboratory, EPA Region I, EPA Las Vegas, Battelle Columbus, Washington State University, Interstate Sanitation Commission, New York State Department of Environmental Conservation, and the University of North Carolina. Discussed were preliminary results of ozone measurements collected during a study conducted to investigate transport phenomena in the Northeastern United States. The study was undertaken to investigate the extent and importance of transport in this densely populated area. The ultimate purpose of the study was to provide the necessary information needed to determine the suitability of present control strategy.

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PROCEEDINGS OF SYMPOSIUM
ON
1975 NORTHEAST OXIDANT TRANSPORT STUDY

Research Triangle Park, North Carolina
January 20-21, 1976

1. INTRODUCTION

Joseph J. Bufalini and William A. Lonneman
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On January 20-21, 1976, a symposium was conducted in Research Triangle Park, NC, to present preliminary results of an oxidant transport study performed during the summer months of July and August 1975 in the New England area. These studies were conducted by the U.S. Environmental Protection Agency (EPA) and EPA-funded research teams to investigate ozone and ozone-precursor transport in the highly populated and highly polluted source areas of the northeast.

The study was organized in response to an EPA Region I request to investigate high nighttime ozone levels at several sampling sites throughout Region I, apparently the result of transport from upwind sources located southwest of Region I. These observations bring in question the effectiveness of a local transportation control strategy if high ozone concentrations are the result of upwind sources. Since previous studies conducted in the midwest during the summer months of 1974 show ozone and ozone-precursor transport as a real problem the necessity of a regionwide or, in the case of the highly populated northeast, a multiregion control strategy is suggested.

The January 20-21 symposium consisted primarily of the presentation of preliminary field study results by the principal investigators involved in the northeast study. This includes sampling programs conducted in both EPA Regions I and II. Also included in the symposium were presentations of results from pertinent laboratory experiments funded by EPA to investigate the ozone potential of simplified surrogated hydrocarbon and nitrogen oxide mixtures in outdoor irradiation chambers. The principal features of these studies were the investigation of long-term irradiation effects and ozone potential of these surrogated mixtures during second and third day irradiations.

In addition to the northeast study, results were presented from other ozone transport studies conducted during the summer months at other areas of the United States. These include following a high pressure system from its formation in the northwest as it moves south and eastwardly. During these high pressure movements, concentrations of ozone and its precursors increase due to the passage of this system over areas of increasing population and anthropogenic activity. The results from a second study conducted in the Houston-Gulf Coast area were also presented. The general purpose of this study was to investigate the relationship of high and low ozone concentrations and associated backward air mass trajectories. A summary of this presentation will not be included in this manuscript; however, an EPA report of the detailed result of these studies is available (EPA-450/3-76-033, The Formation and Transport of Oxidant along Gulf Coast and Northern United States).

During the course of the meeting, a short impromtu presentation was made of an active EPA contract by Mr. Phillip Youngblood. This contract was designed to determine the relationship of oxidant levels to meteorological features. The data used for this contract consisted of available data from previous field study activities. Mr. Youngblood reported that the measurement of Sr^{90} in the atmosphere suggests that stratospheric intrusion of ozone is minimal.

There were two aspects of this study that were not covered in the meeting of January 20-21. These were (1) the possibility of using tracers for the 1975 study and (2) the plant damage study done by Dr. John Spengler (Harvard University, School of Public Health).

During the numerous meetings held both in Research Triangle Park, NC, and Boston, MA, before the study was undertaken, we had discussed the use of tracers to better follow air trajectories into the Region. Since SF_6 had been used in the past, we thought that this compound could be considered as a possible candidate for tracer work. However, after talking to Mr. Gil Ferber of the National Oceanographic and Atmospheric Administration (NOAA) at Rockville, MD, we concluded that SF_6 would not be a suitable tracer. The reason for this is that Mr. Ferber conducted a study in 1971 and found that the SF_6 concentration varied from 10^{-13} to 10^{-12} (v/v). His studies extended from New England to the Carolinas and as far west as Chicago. Many local sources of SF_6 were detected, and it was impossible to determine a single plume.

Since SF_6 was apparently unsatisfactory as a tracer, we then discussed the possibility of using natural emissions of nuclear reactor power plants. Xenon 133 was considered by Mr. C. Fitzsommons (EPA-Las Vegas). Within the states of New Jersey, New York, Connecticut, Massachusetts, and Vermont, there are five power reactors that emit radioactive noble gas. However, according to Mr. Fitzsommons, the samples have to be cryogenically separated and subsequently counted with a scintillation spectrometer. The separation takes 2 to 3 hours. Because of the extremely tight schedule for the Las Vegas B-26 aircraft, it was decided not to burden the personnel with the extra heavy work schedule entailed in Xenon 133 analyses.

One last attempt was made to use tracers. This was to contact Metronics Associates to investigate the possible use of fluorescent particles. The cost for the study was much too high, and it was then decided to abandon the use of tracers for the 1975 Oxidant Study.

Ms. M. Drucker (EPA Region I) suggested early in the study that Dr. Spengler was interested in the study and that it might be mutually beneficial if the various groups (Washington State University, Battelle, EPA) took care of some tobacco plants for Dr. Spengler. Plants were sent to the groups by Dr. Spengler, and the three groups were to water and visually inspect the plants every day. Although we neglected to invite Dr. Spengler to the Conference, Dr. Spengler graciously consented to supply a manuscript of his findings.

2. OPENING REMARKS

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We first became aware of the possibility of high ozone in areas downwind from major cities (rural areas) through our chamber studies in the middle sixties. At that time, it was noticed that high ozone/oxidant concentrations could be obtained by irradiating HC and NO_x mixtures for a second day, i.e., a so-called reacted hydrocarbon-NO_x mixture could be irradiated a second day (after sitting overnight) and produce a significant quantity of ozone. Another observation that was made with these chamber studies was that very little hydrocarbon and almost no oxides of nitrogen were needed to produce oxidant concentrations greater than 0.1 ppm. This was accepted and explained by smog chamber specialists as the "dirty chamber effect." Chamber studies also showed that the so-called least reactive hydrocarbons also produced high concentrations of ozone when high hydrocarbon/NO_x ratios were employed. This observation is especially relevant to ozone and ozone-precursor transport since this is the condition that would be expected in rural areas. The reactive hydrocarbons, i.e., the olefins, are expected to have reacted almost completely. The aromatics should for the most part also be gone. The only remaining hydrocarbons are the paraffins. Since most of the NO_x has also reacted, the conditions are appropriate for having the paraffins under conditions of maximum reactivity for ozone production. Also relevant here are the findings of the old CAPI-6 group. This group consisted of smog chamber specialists that used their chambers to check out the reactivity of certain hydrocarbons. The stability of ozone in the chambers was also tested. The results showed that ozone could have a rather long half-life even when the lights are turned on.

What does all this have to do with ozone transport? Well, all of the information was here in the smog chamber data. The smog chambers showed (1) very little HC is needed for O_3 production with almost no NO_x, (2) the so-called unreactive hydrocarbons could produce ozone at a high HC/NO_x ratio, and (3) ozone, once produced, would be quite stable and would stay around a long time. All that was needed was an experiment to test the hypothesis that high O_3 could be expected downwind from major cities. However, since our interests at that time (middle to late sixties) were concentrated on the measurement of the air quality in various cities (mostly Los Angeles and New York), no such experiments were performed.

At that time, the only evidence that ozone and ozone precursors could travel at least a moderate distance was the data from Riverside, CA. In Riverside, two ozone maximums are observed: one between 11 a.m. and 1 p.m. and the other later in the afternoon (4 to 6 p.m.). Those of you that have heard Dr. Jim Pitts speak on this subject well remember his slides. The slides show the smog as it travels from Los Angeles to Riverside. In the last few years, there have been reports of high ozone in Palm Springs and also Indio. These cities are approximately 110 and 130 miles away from downtown Los Angeles.

Most people have accepted the fact that the Los Angeles Basin is unique. Pollutants really cannot go anywhere, and that is the reason for the smog. However, in the late sixties and early seventies, the Mt. Storm, WV, Christmas tree incident arose. This area in West Virginia is approximately 80 miles away from a large city, (Pittsburgh, PA). A thorough study by the Research Triangle Institute, with Environmental Protection Agency funding, indicates that the Christmas tree damage arose from high levels of ozone. The high ozone levels in this area are attributed to ozone and ozone-precursor transport from upwind sources.

Since the Mt. Storm incident, a number of reports have appeared that indicate ozone and ozone precursors can travel great distances. I have reference here to the work of Stasiuk and Coffey in New York State and that done by EPA Region IV in Florida.

In 1973, EPA awarded a contract to Washington State University (Westburg and Reamussen) to look at the oxidant transport problem. Our thoughts were to have several different cities studied. This was to be done by ground level stations and by aircraft. Two cities that were investigated in 1973 were Phoenix, AR, and Houston, TX. In the Phoenix study, the ozone levels found by the aircraft at 1000 feet above ground level were ∿ 50 to 60 ppb upwind of the city. Downwind (6 to 10 miles), the ozone levels would increase to 100 to 140 ppb. After 30 to 40 miles downwind, the ozone would again decrease to 60 to 70 ppb. In Houston, some unusual observations were made. The ozone levels were found to be 110 to 130 ppb at 30 to 40 miles upwind of the center of the city. At 10 miles downwind, 330 ppb was observed, and some 40 miles downwind, the O_3 levels decreased to 120 to 180 ppb. What was apparently happening in Houston was that the ozone levels were high even before pollutants were picked up from the city. The city did have a significant effect on the O_3 levels, but this was for only short distances (30 to 40 miles).

In 1974, EPA took part in a study in which the entire midwestern area of the United States was covered with three aircraft situated in the Ohio cities of Wilmington, Canton, and Dayton. The findings of the 1974 study were: (1) the oxidant standard is exceeded in rural areas more than in urban areas, (2) area pollution extends beyond a radius of 150 miles, (3) a major urban area has an observable influence on the order of 30 to 50 miles downwind, and (4) when a region is under the influence of a synoptic high pressure system, i.e., a region characterized by clear skies and a weak disorganized flow, high ozone levels can be expected.

The results of last year's research program imply that control of hydrocarbons from any individual city will reduce but not necessarily prevent high concentrations of ozone. The data suggest that controls must be considered on a regional level. Controls must also be considered for oxides of nitrogen.

This past summer (1975) we undertook an oxidant transport study in New England. This study was undertaken at the request of EPA Region I. The Region had complained that they could not implement control plans since the high ozone levels that were observed suggested nonlocal sources. A study of their data did indeed suggest this, since high levels of ozone were observed in the late evening or early morning hours. With two contractors (Battelle and Washington State University) along with the EPA Las Vegas aircraft, we covered most of the Northeast. Later in the study (from August 10 to August 21) the Interstate Sanitation Commission, with EPA funding, also participated in the study and performed aircraft sampling measurements of O_3 over Pennsylvania, New York, and New Jersey.

3. OZONE AND OTHER POLLUTANTS MEASURED BY WASHINGTON STATE UNIVERSITY DURING THE 1975 NORTHEAST OXIDANT TRANSPORT STUDY

H. Westberg
Washington State University
Pullman, WA

This presentation, which concerns Washington State University's part in the 1975 New England oxidant study, can be divided roughly into three parts: (1) a review of program objectives, including some of the specific goals; (2) a brief description of how our phase of the program was designed to accomplish these goals; and (3) a look at data relevant to various aspects of oxidant production and transport in southern New England.

The primary objectives of the program were:

1. Monitor ozone and ozone precursors over the entire southern New England region.
2. Provide an in-depth analysis of ozone transport into and within the New England region.

The first objective has been completed; interpretation of the data collected is just beginning.

The following list indicates specific areas of interest; it is not complete, but shows those areas most important to our part of the study.

1. Oxidant formation and transport within urban plumes.
2. Oxidant behavior during stagnation periods.
3. Coastal seabreeze effect on oxidant levels.
4. Relationships between oxidant levels and inversion layers.
5. Weekend ozone behavior.
6. Ozone transport in the Connecticut River Valley.

Oxidant formation and transport in the plumes emanating from New York City and Boston were of prime interest. Later in this presentation, data will be shown concerning this aspect of the program. I will also be describing oxidant behavior in relation to passage of high pressure systems through the region (stagnation periods). In addition, data relevant to specific interests 3 and 4 will be mentioned.

In order to satisfy the sampling objectives of the program, a triangular network of monitoring base stations was set up in southern New England. This is shown on the map in Figure 3-1.

We were located on the southern Connecticut coast south of Groton. Battelle's base of operations was near Simsbury, CN, and the two EPA groups were in the Boston vicinity. It was felt a triangular design such as this provided optimum coverage of the study area. Washington State University had access to air masses that originated in the New York City area and moved out over the Atlantic Ocean and Long Island Sound. Battelle could monitor air parcels coming into the region from the northwest, while the EPA groups were positioned to provide upwind and downwind coverage of the Boston metropolitan area.

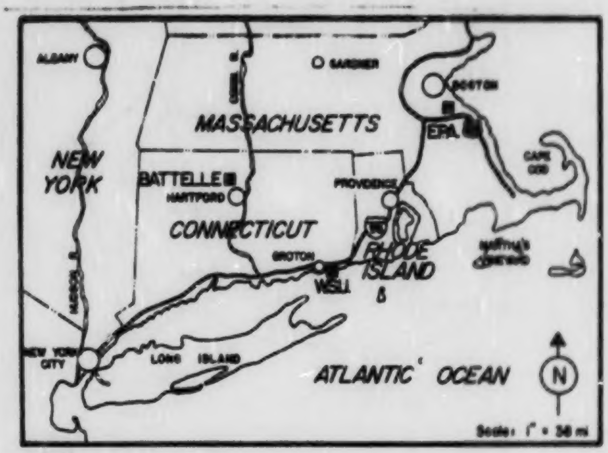

ALBANY
GARDNER
BOSTON
MASSACHUSETTS
EPA
NEW YORK
BATTELLE
HARTFORD
PROVIDENCE
CAPE COD
CONNECTICUT
GROTON
RHODE ISLAND
WSU
MARTHA'S VINEYARD
HUDSON R.
NEW YORK CITY
LONG ISLAND
ATLANTIC OCEAN
N
Scale: 1" = 38 mi

Figure 3-1. Geographic location of special study groups for 1975 Northeast Oxidant Transport Study.

Our main sampling trailer was located near the tip of Avery Point south of Groton (see Figure 3-2). The close proximity of the trailer and airport made it possible to fly low passes for cross-checking the airborne and ground ozone instruments. We also collected bag samples for hydrocarbon analysis at a rural inland site northwest of Groton. This was near the Devil's Hopyard State Park about halfway between Groton and Hartford.

Aircraft flight paths were designed to provide maximum coverage of the southern New England region. During the first half of the study period when two airplanes were operating, we concentrated on the eastern portion of the region. We flew north from Groton to the proximity of the Massachusetts border and then headed east toward Boston (see Figure 3-3). The section of this first leg from Putnam to the turn point overlapped with Battelle's flight path and thus allowed cross-checking of instruments in the two aircraft. The remainder of our route consisted of a counterclockwise arc of 18 miles radius around Boston followed by return to Groton via Providence, RI. Vertical profiles were flown at two points along the flight path. The location of these soundings was generally in an area upwind and downwind of Boston.

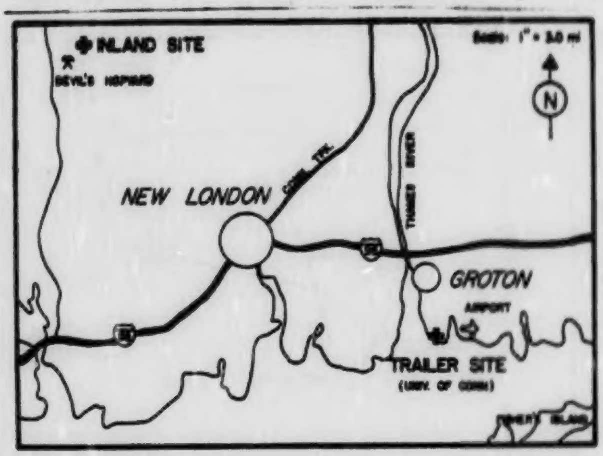

INLAND SITE
DEVIL'S HOPYARD
Scale: 1" = 3.0 mi
N
CONN. TPK.
NEW LONDON
THAMES RIVER
GROTON
AIRPORT
TRAILER SITE
(UNIV. OF CONN.)

Figure 3-2. Location of Groton study site.

When not flying the Boston loop, we generally covered an area south of Groton as shown in Figure 3-4. The objective here was to monitor pollutant behavior over water.

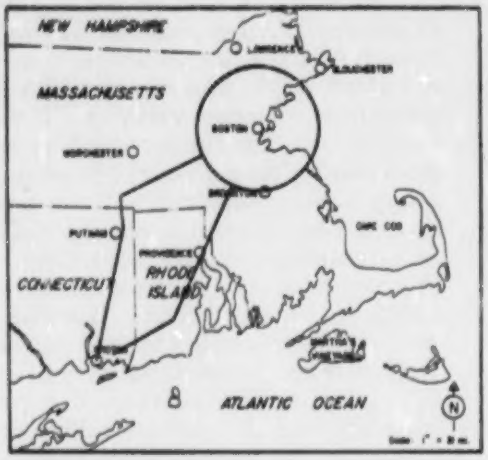

NEW HAMPSHIRE
MASSACHUSETTS
BOSTON
WORCESTER
PUTNAM
PROVIDENCE
RHODE ISLAND
CONNECTICUT
CAPE COD
ATLANTIC OCEAN
N

Figure 3-3. Aircraft flight pattern for Boston Loop.

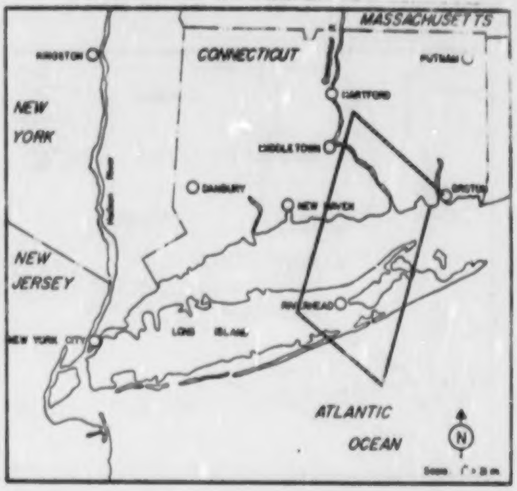

MASSACHUSETTS
CONNECTICUT
PUTNAM
HARTFORD
MIDDLETOWN
NEW YORK
DANBURY
NEW HAVEN
GROTON
NEW JERSEY
NEW YORK CITY
LONG ISLAND
RIVERHEAD
ATLANTIC
OCEAN
N

Figure 3-4. Aircraft flight pattern for South Boston flights.

In early August when the EPA-Las Vegas plane arrived, our primary routes covered the southwestern portion of the region during morning hours and the southeastern area during afternoons. These flight patterns are shown in Figures 3-5 and 3-6.

In concluding this discussion of program design, the Tables 3-1 and 3-2 list the measurements we made. All parameters shown in Table 3-1 were monitored continuously, with the exception of individual light hydrocarbons. These were generally collected over 2-hour periods during morning, afternoon, and evening hours. Not

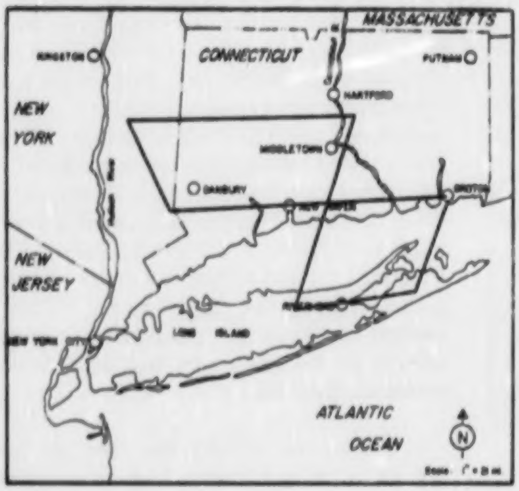

MASSACHUSETTS
CONNECTICUT
PUTNAM
HARTFORD
NEW YORK
MIDDLETOWN
DANBURY
NEW HAVEN
GROTON
NEW JERSEY
NEW YORK CITY
LONG ISLAND
RIVERHEAD
ATLANTIC
OCEAN
N

Figure 3-5. Typical southwestern flight pattern from Groton.

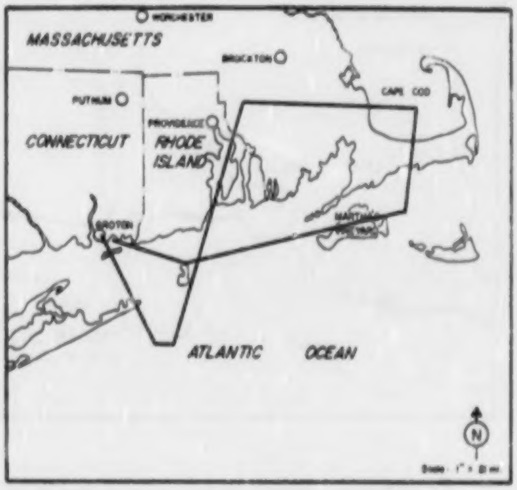

WORCESTER
MASSACHUSETTS
BROCKTON
CAPE COD
PUTNAM
PROVIDENCE
CONNECTICUT
RHODE ISLAND
GROTON
ATLANTIC
OCEAN
N

Figure 3-6. Typical southeastern flight pattern from Groton.

listed in this table is the measurement of upper level winds. This information was obtained from pibal observations each morning and afternoon. Data from aircraft instrumentation (Table 3-2) were continuously recorded on magnetic tape. Bag samples for hydrocarbon analysis were collected at various points along the flight path.

Table 3-1.
GROUND LEVEL MEASUREMENTS

Ozone
Oxides of nitrogen
Total hydrocarbon
Methane
Carbon monoxide
Individual C_2-C_6 HC
Halocarbons
Wind speed
Wind direction
Turbulence
Dew point
Solar radiation
Temperature
Vertical temp. discontinuity (acoustic radar)

Oxidant behavior in the plumes downwind of Boston and New York City was of special interest in this study. The following figures will provide examples of the type of information we collected concerning urban plumes.

On July 22, afternoon winds along the Connecticut coast were from the southwest quadrant. The flight path shown in Figure 3-7 is typical of those used to monitor the area downwind of the New York-New Jersey region under these wind conditions. The numbers shown are ozone levels at specific points along the route. Unless otherwise specified, the flight altitude was near 1000 feet above mean sea level. The aircraft departed Groton about 1: 15 and, heading west, climbed to 7000 feet over New Haven. After spiraling down to 1000 feet, it headed south across Long Island Sound and then southeasterly to a point about 30 miles south of Long Island. As can be seen, ozone levels were generally in the 90- to 100-ppb region up to the southern coast of Long Island, at which point they increase to greater than 140 ppb over the ocean. On the final leg into Groton, this area of elevated ozone was examined more closely by flying a series of vertical profiles across the high ozone region.

The northernmost profile (point g in Figure 3-7) is shown in Figure 3-8. Two temperature inversions are obvious. Note the close correspondence between these temperature discontinuities and the vertical ozone profile. The high ozone concentrations near the surface fall off quite rapidly up to the base of the surface inversion, indicating poor mixing in this region. Between the two temperature breaks, the decrease with altitude is much less. However, the rapid decrease in ozone concentration with altitude is once again apparent above the 3500-foot level.

Figure 3-9 shows the lower portion of the southermost profile in this series (point d in Figure 3-7). The ozone and temperature profiles are similar to that shown in the previous figure, with highest oxidant levels recorded below 1000 feet.

Table 3-2. AIRCRAFT MEASUREMENTS

Ozone
Condensation nuclei
Visual range (nephelometer)
Temperature
Relative humidity
Navigational parameters
Bag/can samples (hydrocarbons, halocarbons, NO_x, etc.)

Shown in Figure 3-10 is a vertical profile in the region between the two shown previously. Ozone levels near the surface are approaching 200 ppb.

To summarize, on this day the region of highest oxidant stretched for approximately 25 miles in the north-south direction and extended from the surface to about 1000 feet. This type of ozone distribution was commonly observed

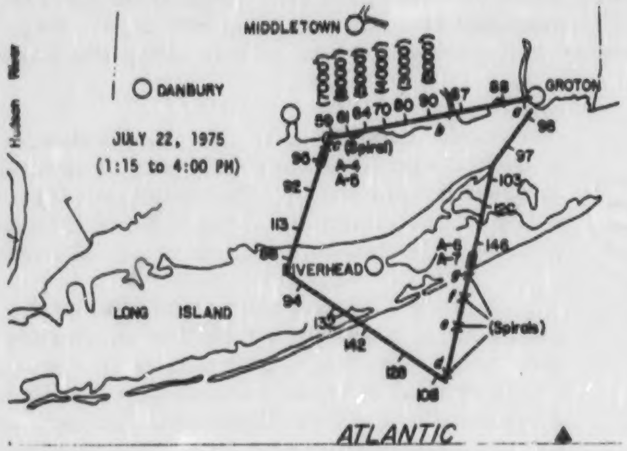

MIDDLETOWN
DANBURY
GROTON
Hudson River
JULY 22, 1975
(1:15 to 4:00 PM)
(7000)
(6000)
(5000)
(4000)
(3000)
(2000)
59
61
64
70
80
90
107
88
98
97
103
120
146
96
92
113
88
94
132
142
128
106
(Spiral)
(Spirals)
A-4
A-5
A-6
A-7
RIVERHEAD
LONG ISLAND
ATLANTIC

Figure 3-7. Ozone results (in ppb) for air-flight downwind of New York - New Jersey area during afternoon hours of July 22, 1975.

over the water when winds were from the west.

The following figures will show additional features of this oxidant plume. On several occasions, the position of the plume was shifted to the north, encompassing the Groton area. July 18 is a good example. Winds on this day were from the southwest.

Figure 3-11 shows oxidant levels for the 4-day period, July 17-20, recorded at our ground trailer site south of Groton. Ozone levels were very low on the 17th, up to about 160 ppb on the 18th, and then back down below 60 ppb on the 19th and 20th. On all four of these days, solar intensity was high.

In Figure 3-12, it can be observed that the burst of ozone on July 18 was accompanied by a simultaneous jump in Freon-11 levels. Other anthropogenic source indicators such as carbon monoxide and acetylene also exhibited coincident concentration increases.

Table 3-3 shows individual light hydrocarbons collected on July 18 at the trailer site. Data are included for the morning and evening hours. Note that hydrocarbon behavior is opposite that normally associated with localized photochemical processes. The substantial increase in hydrocarbon levels from morning to afternoon is indicative of a transport process.

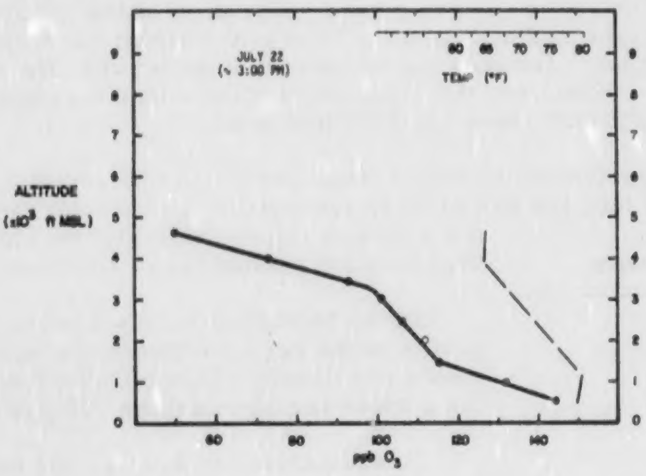


Figure 3-8. Vertical profiles of ozone and temperature over point g (Figure 3-7).

Aircraft flights on July 18 showed once again that the highest ozone levels existed near the surface. This is shown in Figure 3-13. Hydrocarbon concentrations were also highest at lower elevations as shown in Table 3-4. The 500-foot sample was fairly comparable with samples collected on the ground during afternoon hours. Both the ozone and hydrocarbon levels were low at 7000 feet.

On several occasions, our flights around Boston showed elevated ozone levels in the downwind area. An example is the morning flight of August 3, shown in Figure 3-14. Winds were from the northeast. Ozone levels along the upwind section of the arc are in the 35-ppb range, while those in the southwest quadrant (downwind) are up in the 120's. In addition, there was a significant increase in the downwind ozone concentration from 11:00 to 12:30 p.m.

Figure 3-15 shows an expanded view of the southwest portion of the arc. We entered the arc from the northern leg at about 11:00 a.m. As the plane started its counterclockwise circle, ozone concentrations in the 60- to 80-ppb range were recorded. By the time the plane had completed the circle of Boston (approximately 12:30 p.m.), ozone levels in the southwest quadrant had increased by 30 to 40 ppb.

As indicated earlier, oxidant behavior during high pressure periods was an area of specific interest. A high pressure system from the west entered southern New England during the early morning hours of August 9. This system continued to influence the region for 6 days. As can be seen in Figure 3-16, ozone levels at our trailer site in Groton exceeded 100 ppb on each of these days. Wind flow at the 850-mb level was from the northwest throughout most of this period.

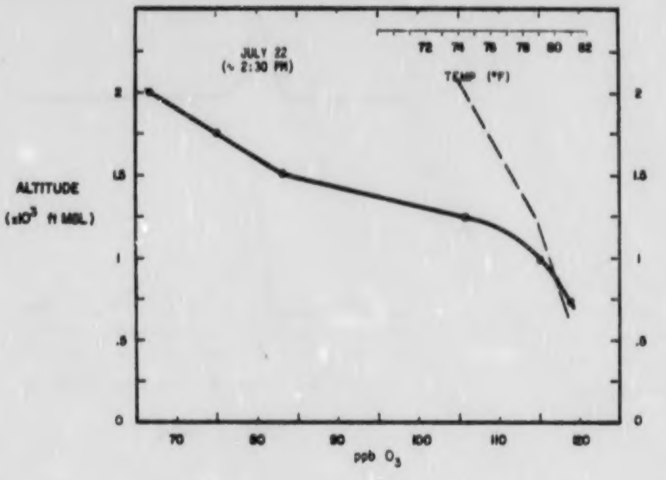


Figure 3-9. Vertical profiles of ozone and temperature over point d (Figure 3-7).

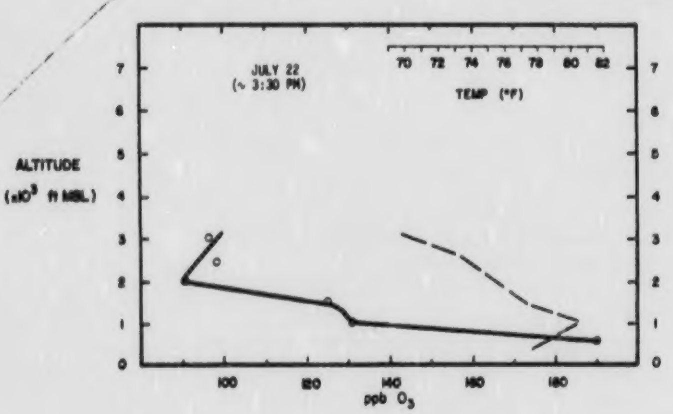


Figure 3-10. Vertical profiles of ozone and temperature between points d and g (Figure 3-7).

The days of August 10 and 13 are interesting in that the normal diurnal ozone patterns are distorted by late evening peaks. Figure 3-17 shows expanded views of ozone curves for the 10th and 13th. These nighttime ozone peaks must result from transport into the Groton area. Aircraft data show that the transport process differed somewhat on these two days. On August 10, we flew a cross-sectional pattern perpendicular to the general wind flow. Highest ozone levels were recorded to the south over water (see Figure 3-18). The vertical ozone profile on this afternoon showed the highest levels to be quite close to the surface (see Figure 3-19).

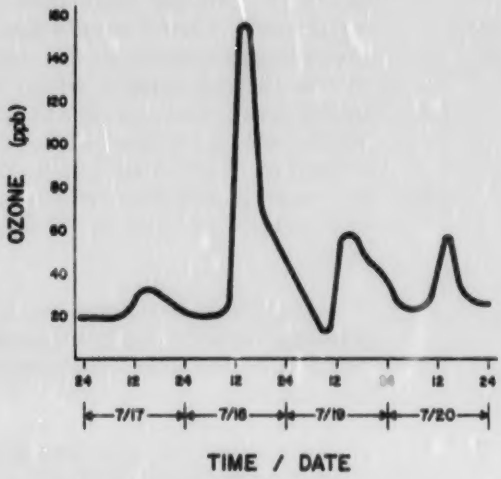


Figure 3-11. Diurnal ozone patterns at Groton ground site during July 17-20, 1975.

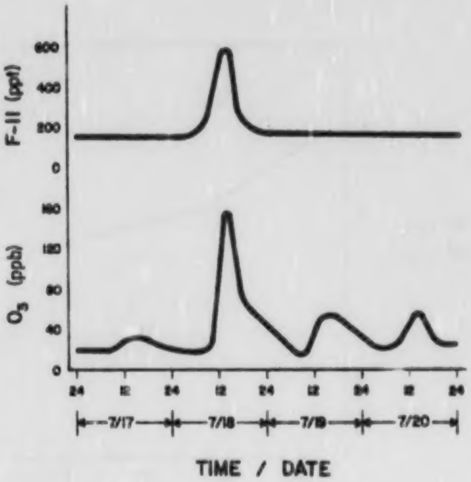


Figure 3-12. Diurnal profiles for ozone and Freon-11 at Groton ground site during July 17-20, 1975.

Table 3-3. HYDROCARBON MEASUREMENTS ($\mu g/m^3$) AT TRAILER SITE ON JULY 18, 1975

	6-9 a.m.	11 a.m.	1 p.m.	9 p.m.
Ethane	4.0	6.5	9.5	4.0
Ethylene	7.5	3.0	4.5	1.5
Acetylene	1.0	2.0	4.0	1.0
Propane	4.0	9.0	10.5	2.0
Propene	3.0	2.0	1.5	0.5
i-Butane	2.0	8.0	10.5	1.0
n-Butane	3.5	11.0	17.0	3.0
i-Pentane	4.0	10.0	16.5	4.0
n-Pentane	3.0	6.0	9.0	2.5
Total	32	58	83	20

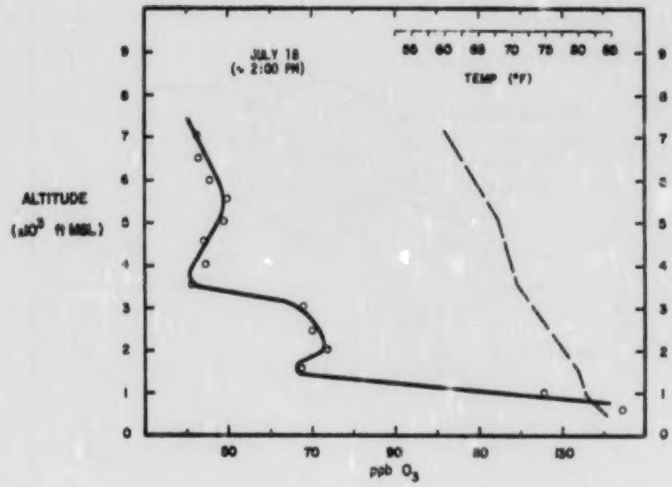


Figure 3-13. Vertical profiles for ozone and temperature over Groton during afternoon of July 17-20, 1975

Table 3-4. AIRCRAFT HYDROCARBON MEASUREMENTS ($\mu g/m^3$) NEAR GROTON (2-4 p.m.) July 18, 1975

	500 feet	2500 feet	7000 feet
Ethane	7.0	5.5	4.0
Ethylene	5.0	5.5	2.0
Acetylene	7.0	3.5	< 0.5
Propane	7.5	5.0	2.0
Propene	2.0	< 0.5	< 0.5
i-Butane	5.5	5.0	1.0
n-Butane	11.5	11.0	1.5
i-Pentane	9.5	8.0	1.5
n-Pentane	5.0	4.0	1.0
Total	60	48	13

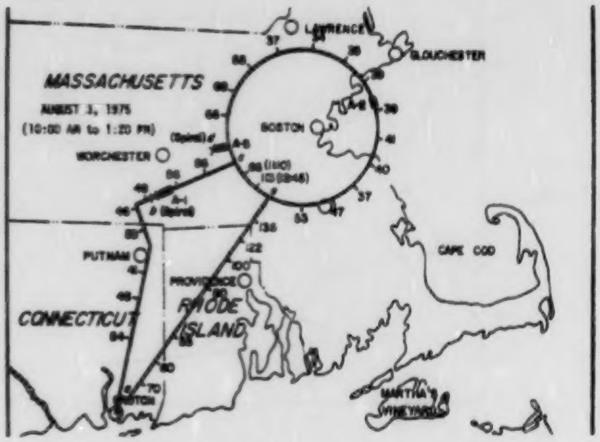

MASSACHUSETTS
AUGUST 3, 1975
(10:00 AM to 1:20 PM)
LAWRENCE
GLOUCHESTER
BOSTON
WORCHESTER
PUTNAM
PROVIDENCE
CONNECTICUT
RHODE ISLAND
CAPE COD
MARTHA'S VINEYARD
37
37
40
41
136
122
100
70
80

Figure 3-14. Ozone results (in ppb) for morning flight of August 3, 1975.

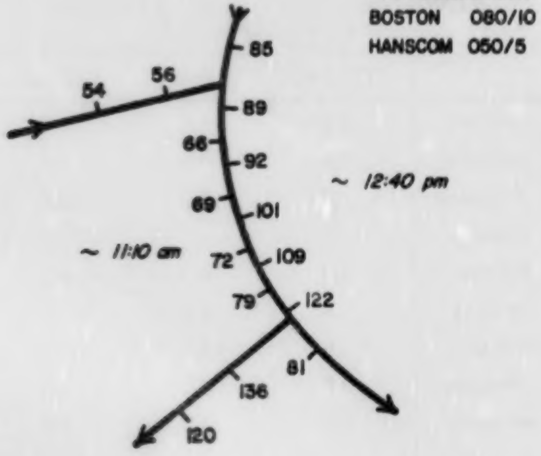

WIND
BOSTON 080/10
HANSCOM 050/5
85
54
56
89
66
92
~ 12:40 pm
69
101
~ 11:10 am
72
109
79
122
81
136
120

Figure 3-15. Expanded view of southwest portion of arc for August 3, 1975 flight (Figure 3-14).

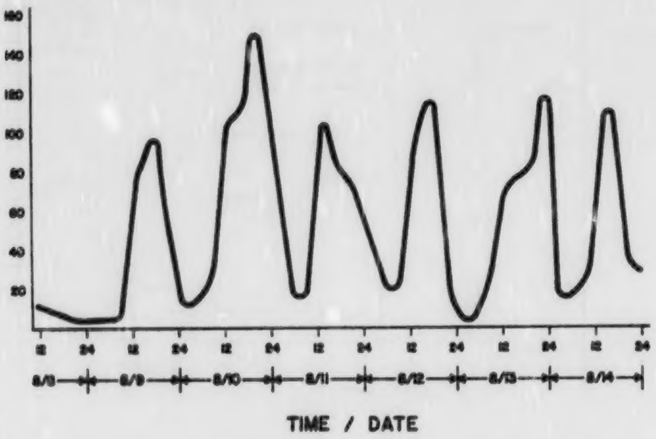


Figure 3-16. Diurnal patterns of ozone (in ppb) at Groton ground site during August 9-14, 1975.

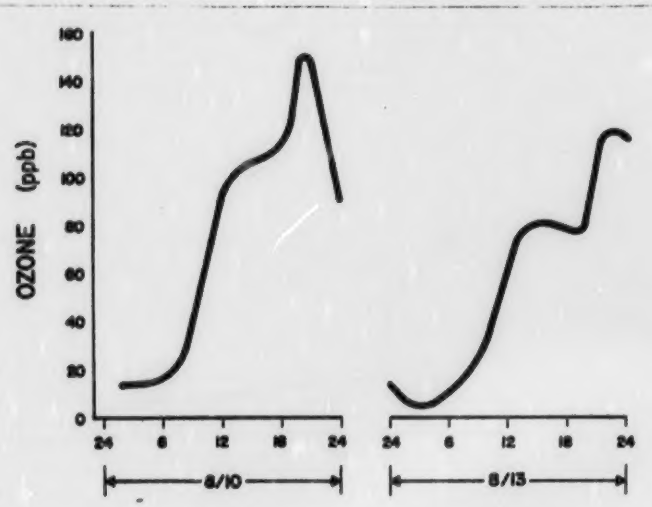


Figure 3-17. Expanded views of diurnal ozone patterns at Groton ground site for August 10 and 13, 1975.

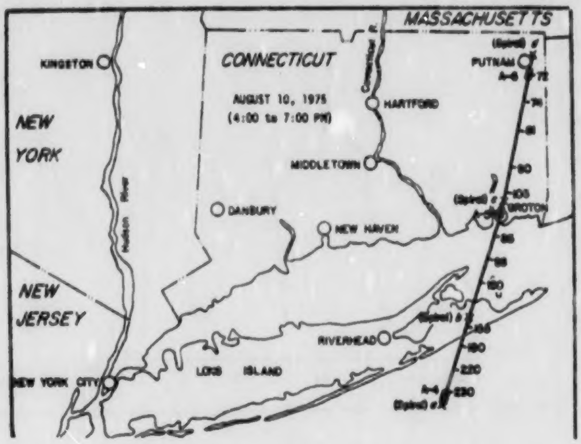

MASSACHUSETTS
CONNECTICUT
AUGUST 10, 1975
(4:00 to 7:00 PM)
KINGSTON
NEW YORK
NEW JERSEY
NEW YORK CITY
HARTFORD
MIDDLETOWN
DANBURY
NEW HAVEN
PUTNAM
GROTON
RIVERHEAD
LONG ISLAND
Hudson River
Connecticut R.
(Spiral)
72
90
105
220
230

Figure 3-18. Ozone results (in ppb) for aircraft flight during late afternoon hours of August 10, 1975.

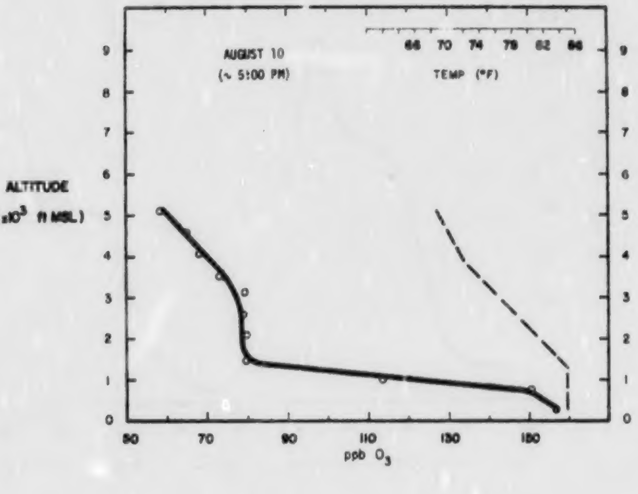


Figure 3-19. Vertical profiles for ozone and temperature near Groton during afternoon hours of August 10, 1975.

4. OZONE AND OTHER POLLUTANTS MEASURED BY BATTELLE DURING THE 1975 NORTHEAST OXIDANT TRANSPORT STUDY

Chester W. Spicer
Battelle Memorial Institute
Columbus, OH

The purpose of the study was, in general, the investigation of the transport of oxidant and its precursors beyond urban areas. In particular, the study was designed to investigate the formation and movement of ozone in the lower atmosphere in and around the New England area. This study was funded entirely by the U.S. Environmental Protection Agency.

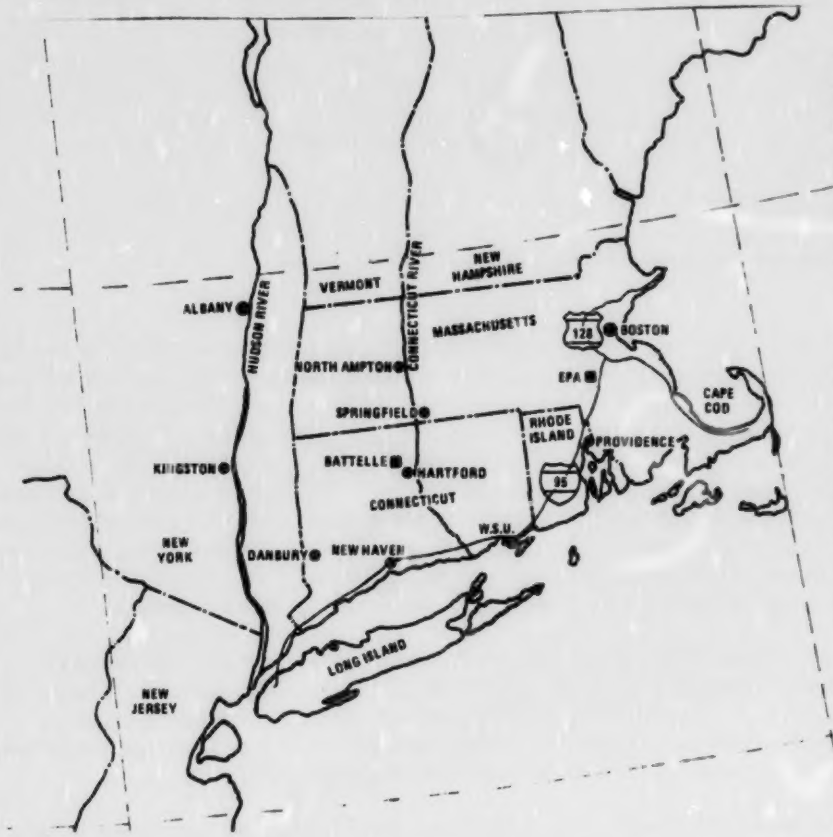

VERMONT
NEW HAMPSHIRE
ALBANY
HUDSON RIVER
CONNECTICUT RIVER
MASSACHUSETTS
128
BOSTON
NORTH AMPTON
EPA
CAPE COD
SPRINGFIELD
RHODE ISLAND
PROVIDENCE
KINGSTON
BATTELLE
HARTFORD
95
CONNECTICUT
W.S.U.
NEW YORK
DANBURY
NEW HAVEN
LONG ISLAND
NEW JERSEY

Figure 4-1. Topographic map of 1975 Oxidant Transport Study area.

Figure 4-1 shows the 1975 Oxidant Transport Study area. The Battelle-Columbus mobile laboratory and aircraft were located at an airport in Simsbury, CN, approximately 15 miles northwest of Hartford.

Table 4-1 shows the meteorological and chemical monitoring techniques used in the Battelle mobile laboratory. The aircraft monitored temperature and ozone (and NO_x on selected flights) continuously. The remaining chemical species were collected in Tedlar bags for subsequent analysis.

We are now just getting the results of our field study data from the computer. These data include 39 days of ground level data from Simsbury and the results from 44 aircraft flights. Figure 4-2 contains the results of the 39-day composite profiles for the meteorological measurements

Table 4-1.
METEOROLOGICAL AND POLLUTANT MEASUREMENTS

Analysis	Instrument
Wind speed and direction	MRI, Model 1074-2 sensor
Temperature	MRI, Model 802 sensor
Relative humidity	MRI, Model 907 sensor
Global radiation intensity	Eppley Lab, 180° pyrheliometer
O_3	REM, Model 612 chemiluminescence monitor
NO NO_x NO_2 (by difference)	Bendix, Model 8101-B chemiluminescence monitor
CH_4 NMHC CO	Union Carbide, Model 3020 automated FID gas chromatograph
C_2H_2 C_2H_4 C_2H_6	Varian Series 1200 gas chromatograph with FID
CCl_3F (Freon -11) CCl_4	Varian Series 1200 gas chromatograph with electron capture detection

made at the Simsbury site. Figure 4-3 contains the 39-day composite profiles for the ozone and nitrogen oxides. Figure 4-4 represent the composite profiles for methane, total nonmethane hydrocarbon, and carbon monoxide. Figure 4-5 illustrates the 39-day composite profiles for ethane, ethylene, acetylene, and propane. It appears that the acetylene and ethylene profiles follow similar patterns, as expected since they have a common source, namely, auto exhaust emissions. Ethane and propane follow different diurnal patterns independent of automotive sources and apparently independent of a common natural gas sources. This is evident during the morning and late evening hours when other sources of propane were observed. Figure 4-6 contains the 39-day composite profiles of ozone, Freon-11, and carbon tetrachloride.

The 39-day composite profiles in Figures 4-2 through 4-6 represent average values observed at the Simsbury site throughout the entire study period. These averages tend to smooth out the day-to-day indications of ozone and other pollutant transport into the Simsbury area; however, they do illustrate the average pollutant profile as well as the general data format of our final report.

Figure 4-7 shows data collected at the Simsbury site during the evening hours of August 11, 1975. The pollutant profiles are plotted over a relatively short time interval to demonstrate the transport of a new air mass into the area. This influx was observed by the sudden changes in the various parameters at 2110. From the figure, it is obvious that high ozone concentrations were observed in this new air mass.

Plots of daily maximum ozone and Freon-11 for the entire study period of July 15 through August 20, 1975, at the Simsbury site are given in Figure 4-8. The close

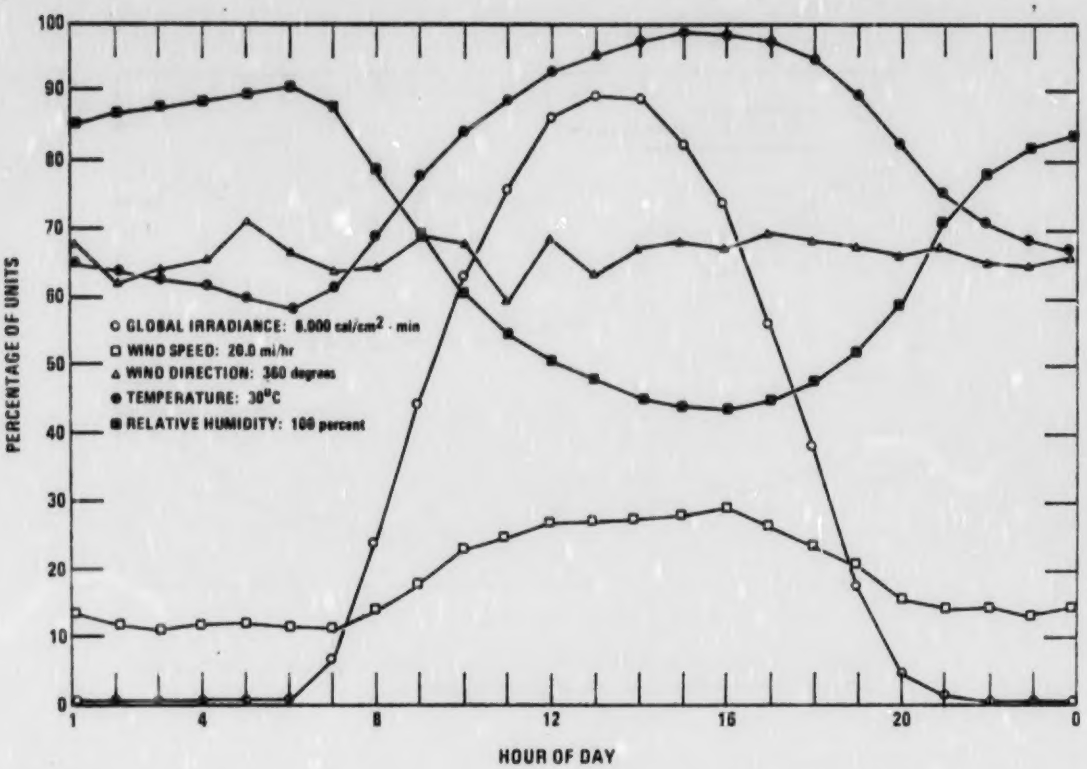


Figure 4-2. Composite profiles for meteorological measurements made at the Simsbury site during the 39-day study period.

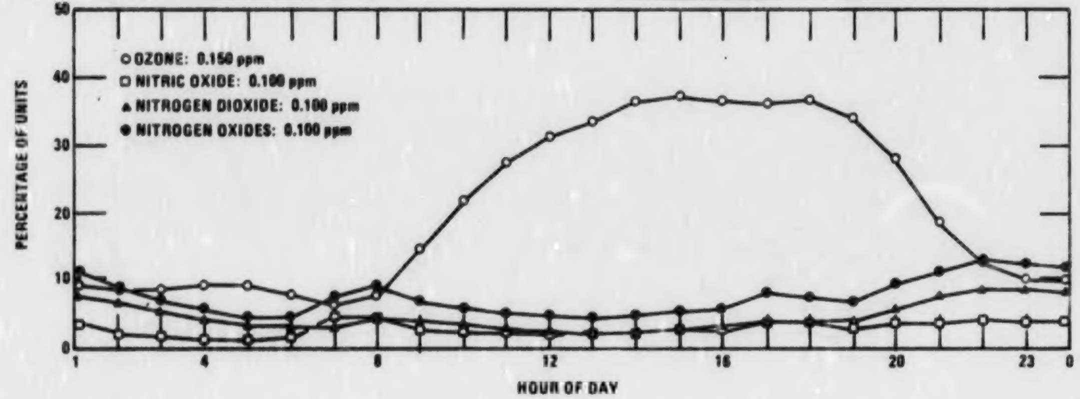


Figure 4-3. Composite profiles for the ozone and nitrogen oxides at the Simsbury site for the 39-day study period.

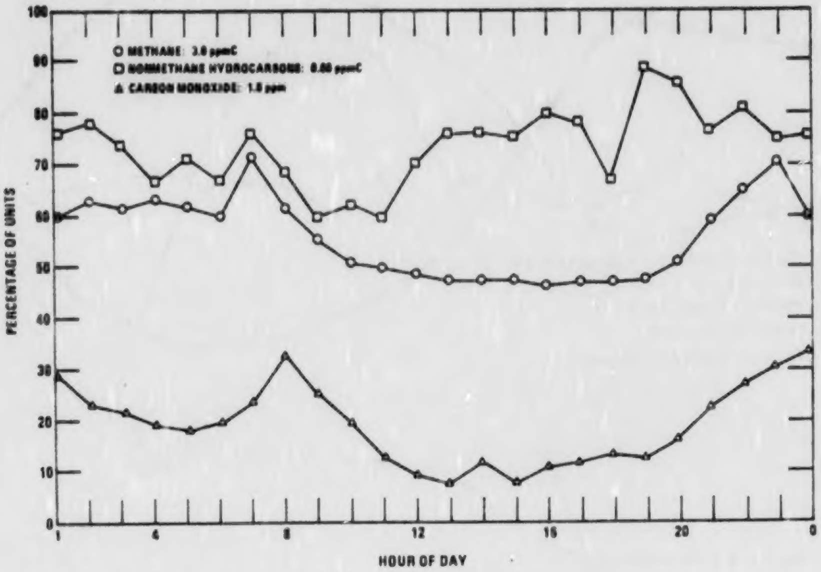


Figure 4-4. Composite profiles for methane, total methane hydrocarbon, and carbon monoxide at Simsbury site for the 39-day study period.

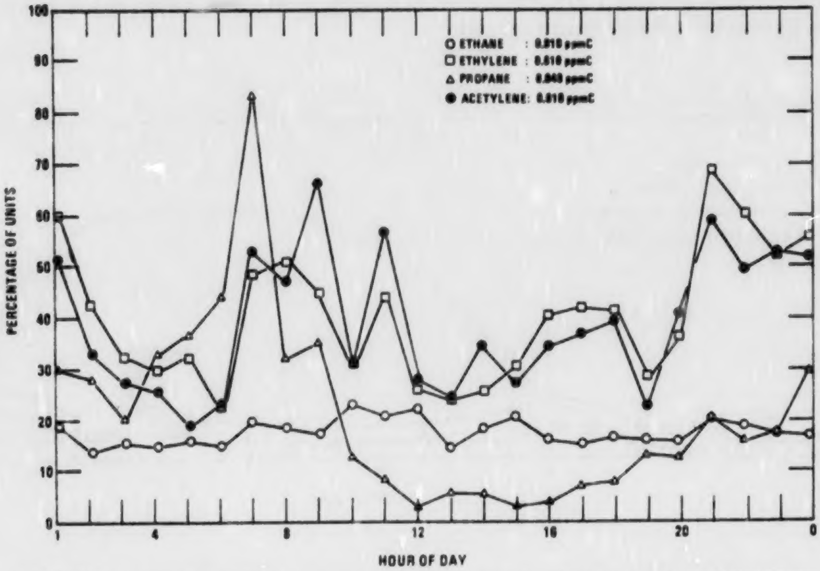


Figure 4-5. Composite profiles for ethane, ethylene, acetylene, and propane at Simsbury site for the 39-day study period.

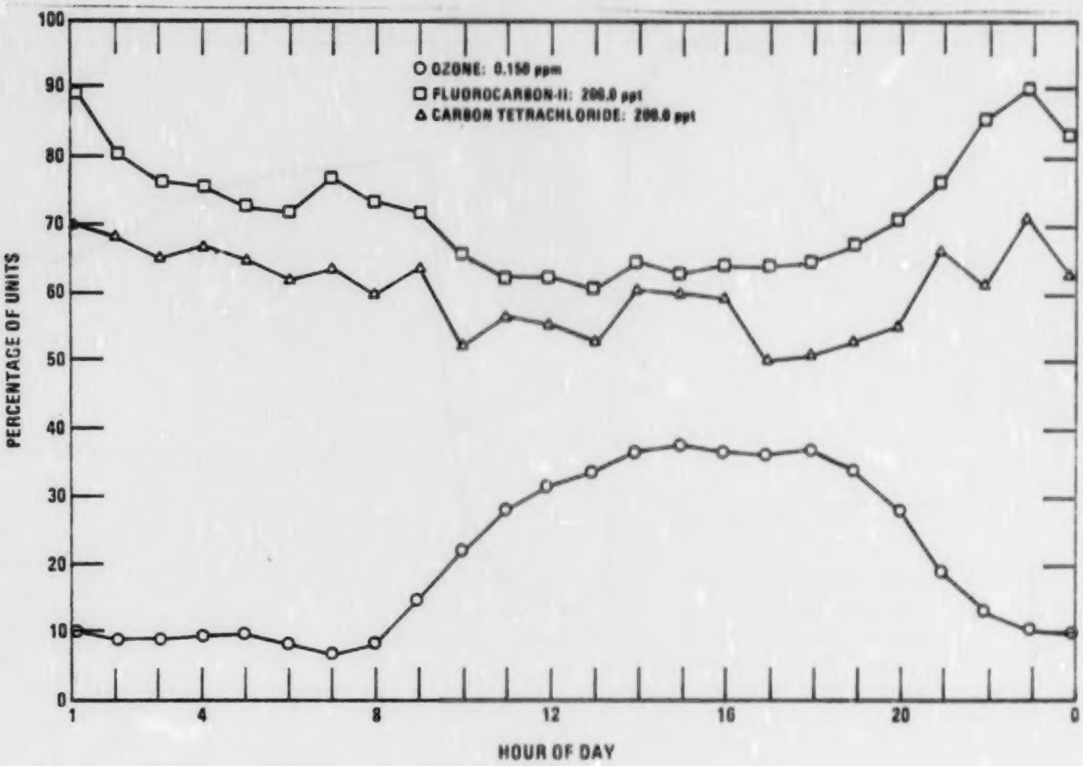


Figure 4-6. Composite profiles for ozone, Freon-11 and carbon-tetrachloride at Simsbury site for the 39-day study period.

correlation between these compounds indicates that much of rural Simsbury's elevated ozone results from the transport of urban air and is, therefore, of anthropogenic origin.

The next group of figures include some of the results obtained from aircraft flights. The flight patterns used during the study were designed to give extended, simultaneous coverage of the entire New England area by two and three aircraft. The flights were also designed to fly special missions which included:

1. Power plume studies.
2. Urban plume transport over ocean bodies.
3. Ozone transport up the Connecticut River Valley.

Figure 4-9 shows the results of a New York urban plume flight for the evening hours of August 9, 1975. Ozone concentrations are plotted versus distance for each sector of the somewhat triangular flight pattern. The number above the plot shows the aircraft altitude for each sector of the flight. The resultant meteorological wind direction is given by the arrow. As can be seen from these plots, elevated levels of ozone were observed 150 miles downwind of the urban area.

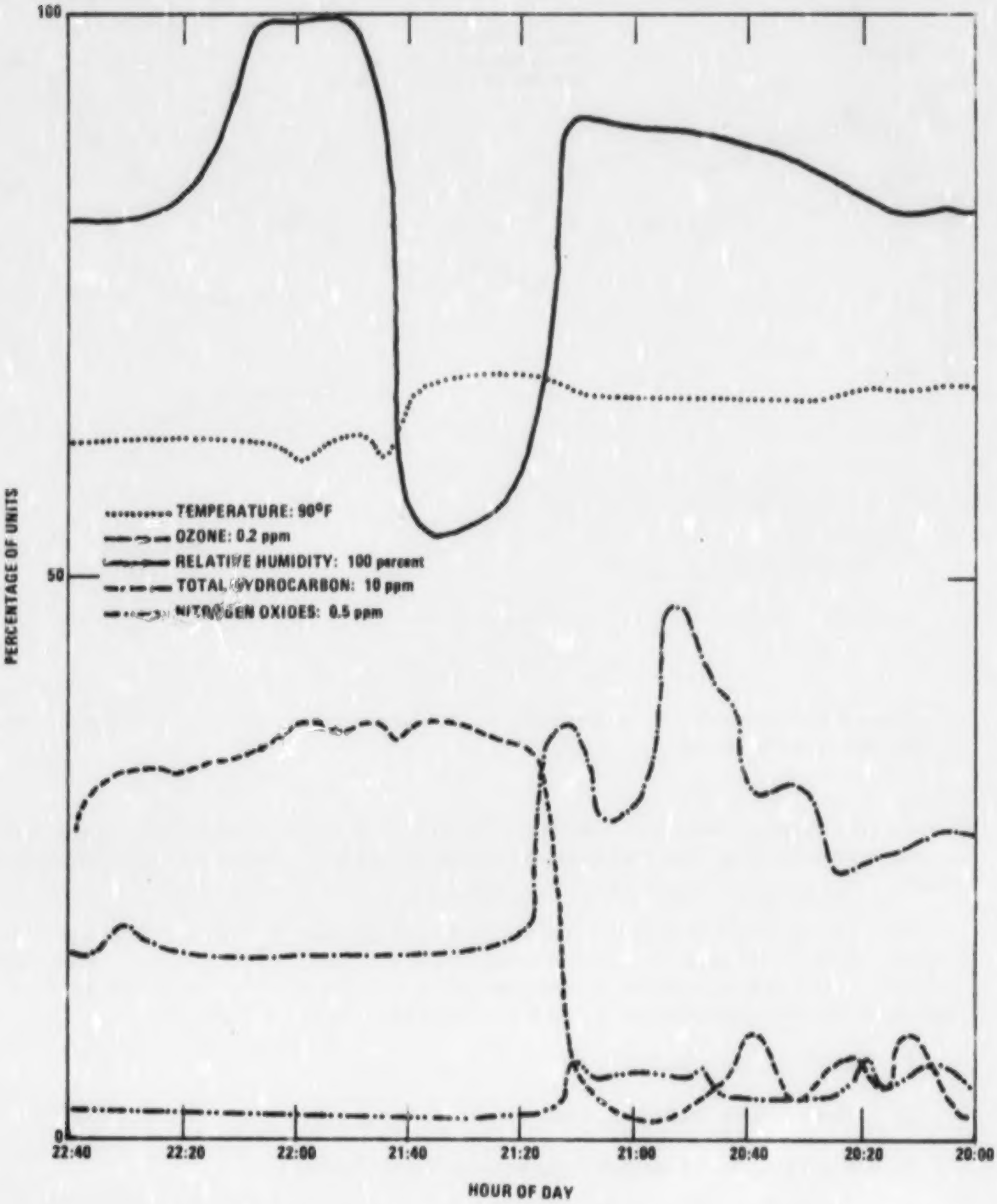


Figure 4-7. Some pollutant and meteorological profiles at 20-minute intervals during evening hours of August 11, 1975.

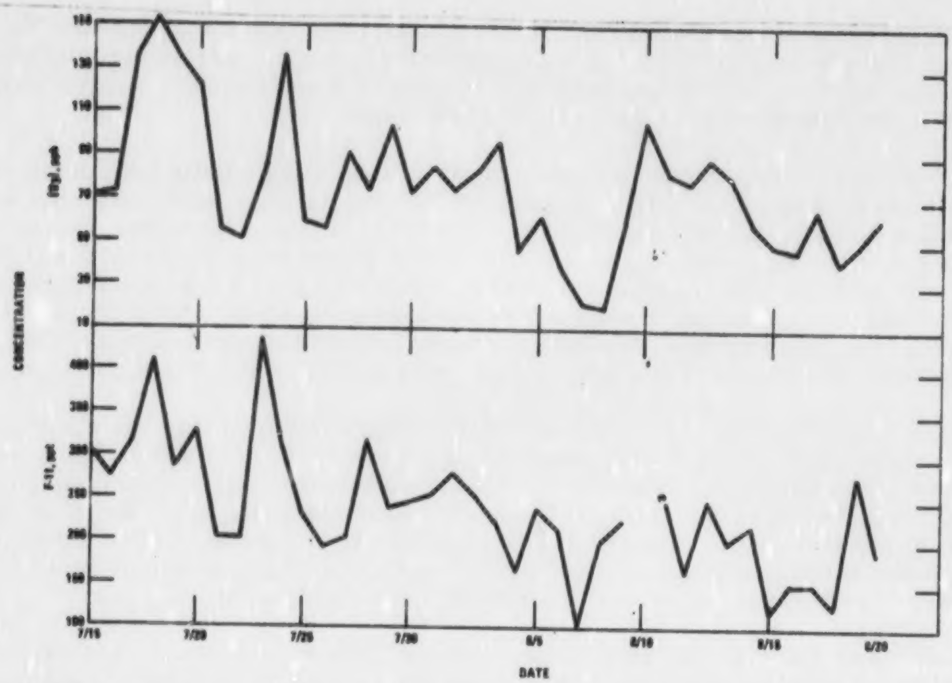


Figure 4-8. Daily maximum ozone and Freon-11 at Simsbury site during July 15-20, 1975.

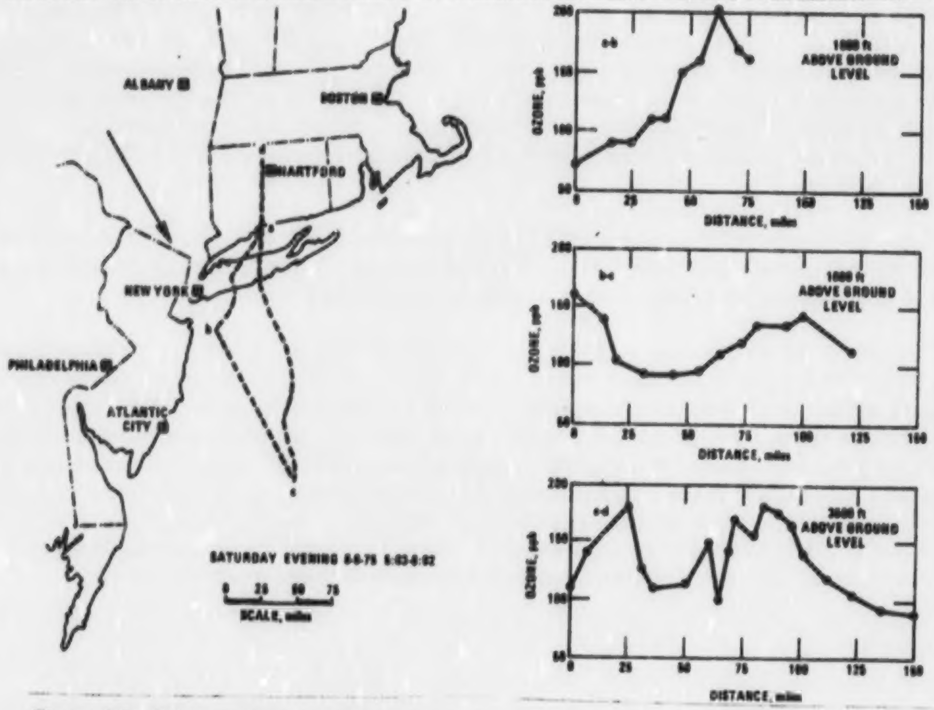

ALBANY
BOSTON
HARTFORD
NEW YORK
PHILADELPHIA
ATLANTIC CITY
a
b
c
d
SATURDAY EVENING 8-9-75 5:03-8:02
0 25 50 75
SCALE, miles
a-b
1000 ft ABOVE GROUND LEVEL
b-c
1000 ft ABOVE GROUND LEVEL
c-d
3000 ft ABOVE GROUND LEVEL
OZONE, ppb
200
150
100
50
0
25
50
75
100
125
150
DISTANCE, miles

Figure 4-9. Flight pattern and ozone results for New York urban plume flight during the evening hours of August 9, 1975.

Vertical profiles of ozone and temperature at the extreme of the New York urban plume flight of August 9 (150 miles downwind of the city) are shown in Figure 4-10. It appears that the ozone and haze both maximize at the base of the inversion. The haze layer determination was a visual observation.

Figure 4-11 represents a Boston urban plume study conducted during the evening hours of August 18, 1975. Concentration results of several pollutants for bag samples collected during the flight are listed in the lower right hand corner. Bag 1 represents the first sample collected; Bag 3, the last sample. From the figure, it is obvious that elevated ozone concentrations exceeding 0.08 ppm were observed as far as 250 miles out over the ocean. As in the New York plume study (Figure 4-9), the aircraft was flown in the same general direction as the meteorological wind direction; therefore, the ozone results depict the effects of downwind urban transport.

The results of a cross-sectional flight pattern flown during the early afternoon hours of August 10, 1975, are reported in Figure 4-12. The winds were continuously from the west during this flight. Again, pollutant results for bag samples collected during the flight are given in the lower right-hand corner. (Bag 1 is the first bag sample along the flight path, Bag 2 is the second, and so on.) Four spirals from the south shore of Long Island to the Massachusetts-Connecticut border were used to determine vertical and horizontal distributional patterns of ozone.

The results from the vertical and horizontal measurements in Figure 4-12 were used to construct a computer-derived density plot of the cross-sectional patterns for ozone as shown in Figure 4-13. The abscissa and right-hand ordinate show horizontal and vertical distances respectively. Ozone concentration is shown by density shading. The number associated with each shading area represents the lowest concentration of ozone. The range of concentration represented by the shaded area is that number up to that concentration associated with the next shaded area. Note that the ozone concentration over the entire horizontal area at approximately 2700 feet is at least 160 ppb, and is in most cases higher than the ground level measurements. Also, the effect of the high ozone precursor sources, the New York City area, is readily evident. In the lower right-hand column, the New York City plume exceeds 200 ppb ozone.

This plot represents the use of horizontal and vertical measurements for only four points at different time intervals. If more simultaneous vertical measurements were made a more precise and detailed picture would be possible.

Figure 4-14 shows vertical O_3 and temperature profiles at two locations on July 27, 1975. The upper profiles were made over central Vermont (rural) and the lower profiles over southwest Connecticut (urban). Note the major differences in the shapes of the ozone profiles. High levels of ozone above 8000 feet over Vermont could be due to stratospheric transport or long distance transport of ozone precursors with upward movement of the air mass. The lower profile shows strong influence of anthropogenic sources below the inversion. A possible regional "background" ozone of 70 ppb associated with a high pressure system over New England is indicated by values above the inversion over Connecticut and values below 8000 feet over Vermont.

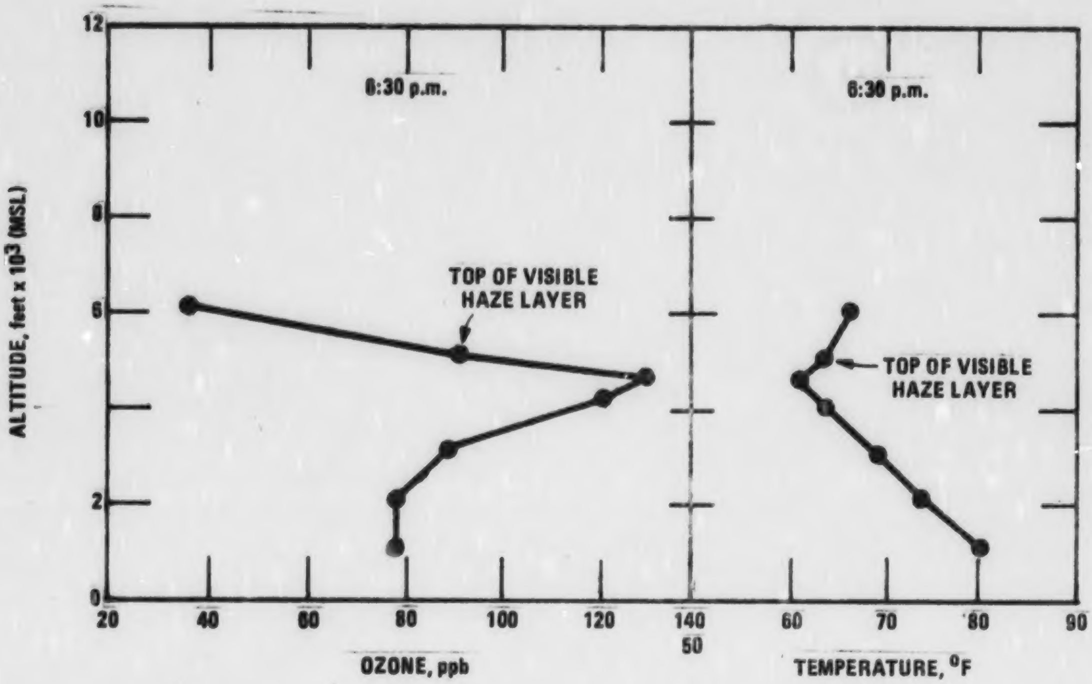
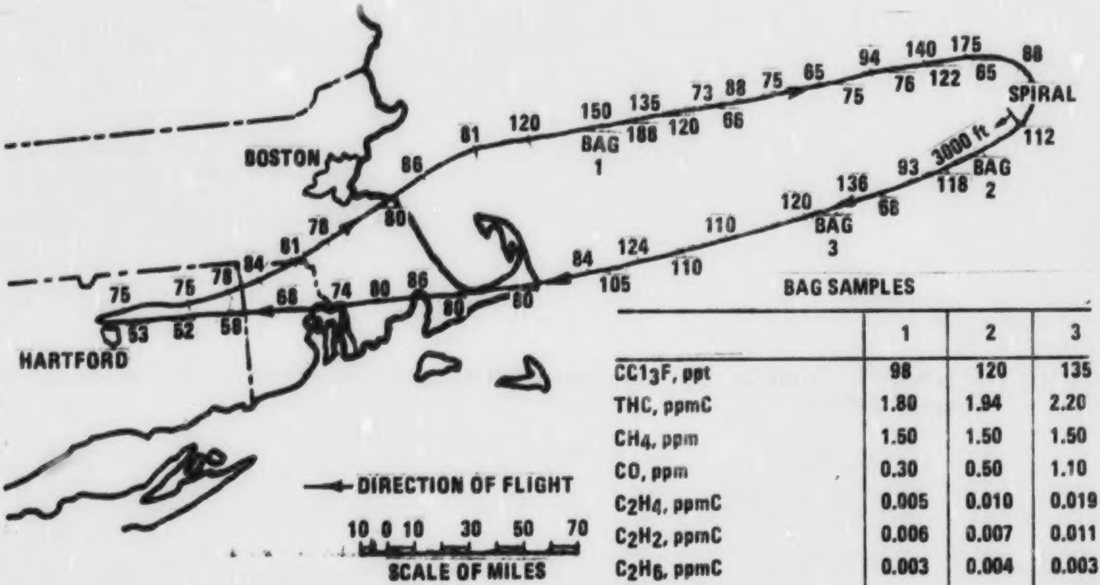


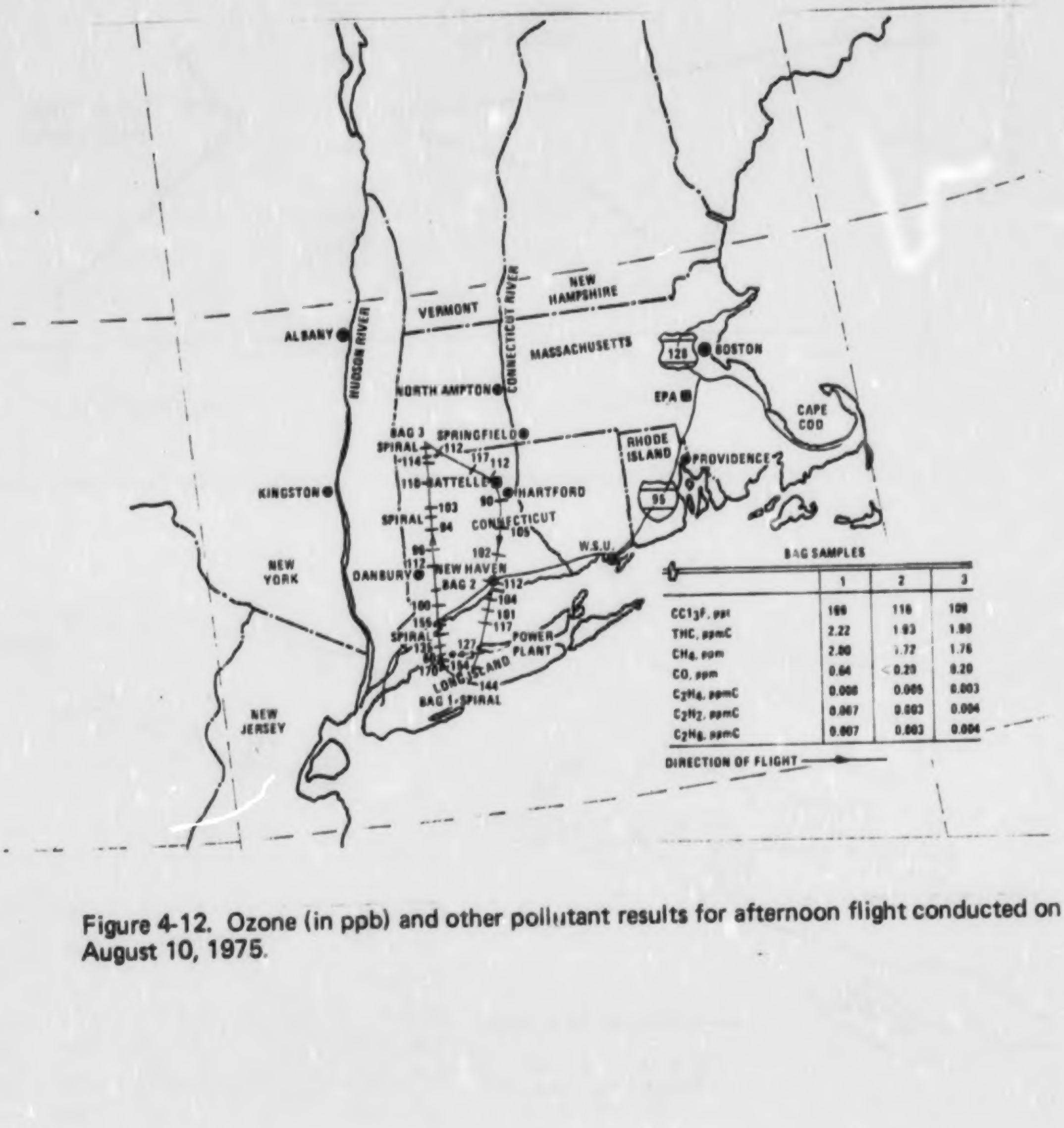
Figure 4-10. Vertical profiles of ozone and temperature at extreme of New York urban plume flight of August 9, 1975.


BOSTON
HARTFORD
SPIRAL
3000 ft
BAG 1
BAG 2
BAG 3
75
75
78
84
81
78
86
81
120
150
135
73
88
75
65
94
140
175
88
75
76
122
65
188
120
66
112
93
136
118
68
120
110
124
84
110
105
66
74
80
86
80
80
53
52
58
80
DIRECTION OF FLIGHT
10 0 10 30 50 70
SCALE OF MILES

BAG SAMPLES

	1	2	3
CCl_3F, ppt	98	120	135
THC, ppmC	1.80	1.94	2.20
CH_4, ppm	1.50	1.50	1.50
CO, ppm	0.30	0.50	1.10
C_2H_4, ppmC	0.005	0.010	0.019
C_2H_2, ppmC	0.006	0.007	0.011
C_2H_6, ppmC	0.003	0.004	0.003
CCl_4, ppt	--	--	150

Figure 4-11. Ozone (in ppb) and other pollutant results for Boston urban plume study conducted during evening hours of August 18, 1975.


NEW HAMPSHIRE
VERMONT
ALBANY
HUDSON RIVER
CONNECTICUT RIVER
MASSACHUSETTS
128
BOSTON
NORTH AMPTON
EPA
CAPE COD
BAG 3
SPIRAL
SPRINGFIELD
112
114
117
112
RHODE ISLAND
PROVIDENCE
110
BATTELLE
KINGSTON
90
HARTFORD
95
103
SPIRAL
94
CONNECTICUT
105
W.S.U.
102
96
112
NEW YORK
DANBURY
NEW HAVEN
BAG 2
112
104
100
101
155
117
SPIRAL
POWER PLANT
135
127
170
154
LONG ISLAND
144
BAG 1-SPIRAL
NEW JERSEY
DIRECTION OF FLIGHT

BAG SAMPLES

	1	2	3
CCl_3F, ppt	166	116	109
THC, ppmC	2.22	1.93	1.90
CH_4, ppm	2.00	1.72	1.76
CO, ppm	0.64	< 0.20	0.20
C_2H_4, ppmC	0.006	0.005	0.003
C_2H_2, ppmC	0.007	0.003	0.004
C_2H_6, ppmC	0.007	0.003	0.004

Figure 4-12. Ozone (in ppb) and other pollutant results for afternoon flight conducted on August 10, 1975.

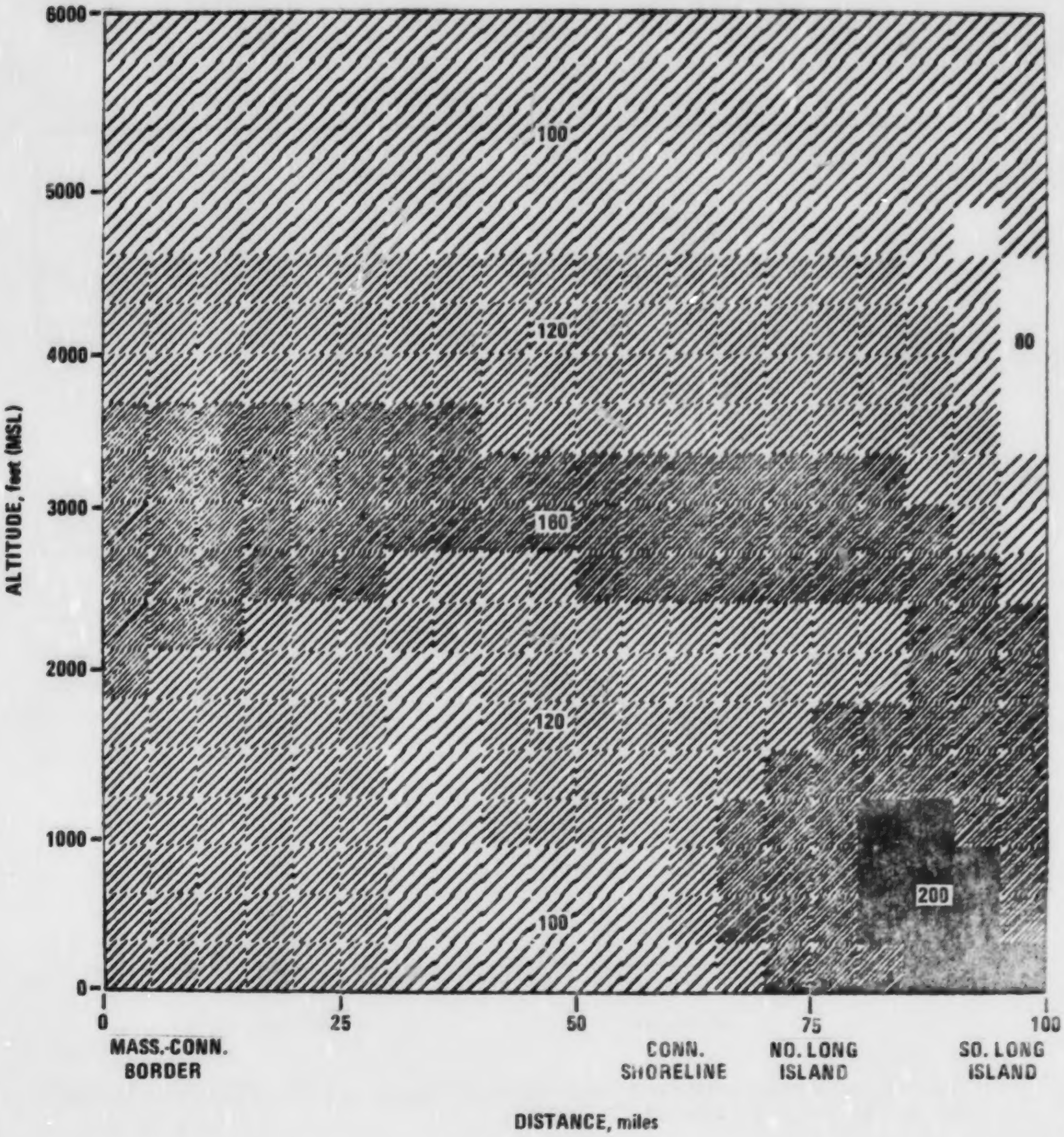


Figure 4-13. Computor-derived density plot of cross-sectional patterns for ozone (ppb) constructed from the vertical and horizontal measurements made during the August 10, 1975 flight (Figure 4-12).

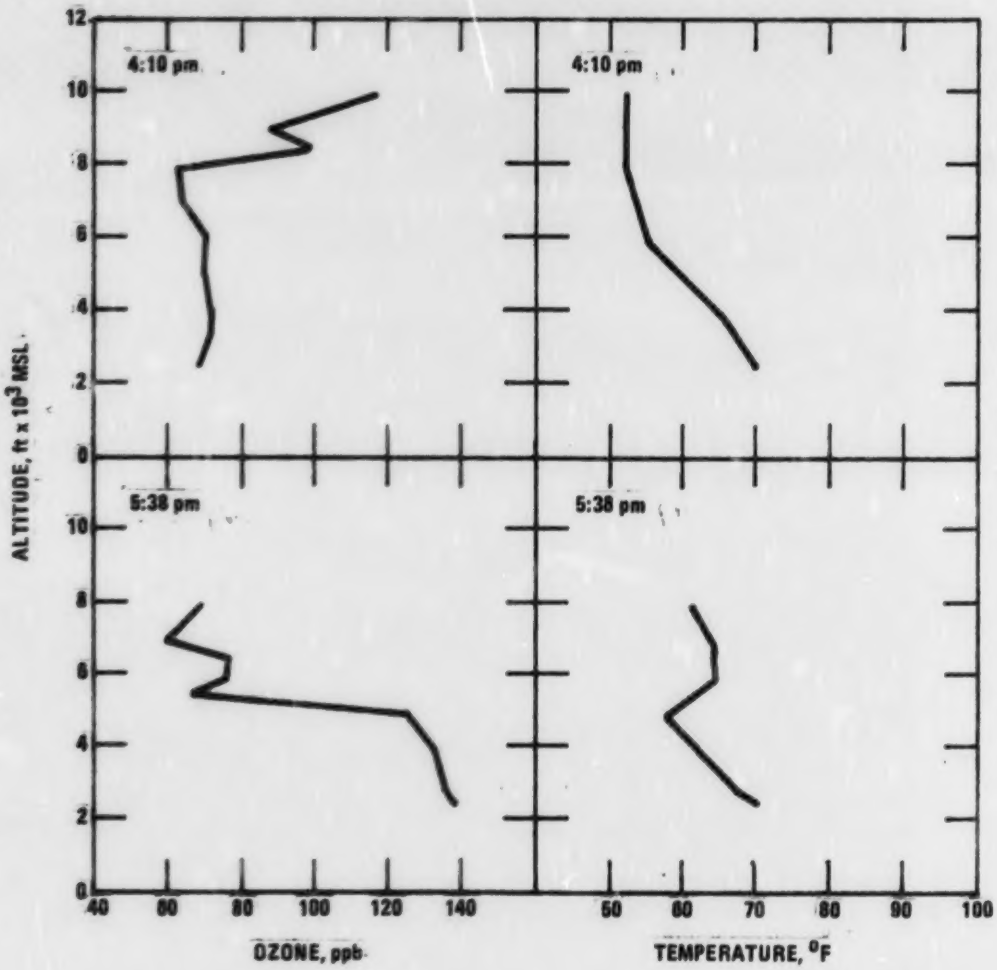


Figure 4-14. Vertical ozone and temperature profiles on July 27, 1975 at sites located in central Vermont and southwest Connecticut.

5. METEOROLOGICAL DATA FOR THE 1975 NORTHEAST OXIDANT TRANSPORT STUDY

Karl F. Zeller
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Las Vegas, NV

Any investigation of oxidant transport requires a simultaneous analysis of the meteorological situation at the time and place of the oxidant observation. Particularly, wind direction will have an effect on the location of high oxidant values, and insolation as well as wind dilution will have an effect on the concentration of the oxidant measured. It is the purpose of this report to provide a reference to the meteorological situation day by day from July 14 through August 29, 1975, as a companion to the oxidant data collected by aircraft monitoring platforms as well as fixed ground monitoring stations in the New England area during the same time period.

A total list of the types and formats of the meteorological data available is given in Table 5-1. Because the total meteorological package would be too voluminous to reproduce, only some basic meteorological information considered sufficient for the analysis of oxidant transport is contained within this report. Examples of this information are listed in Table 5-2 for several sites on July 28, 1975. The data within include the following information:

1. The 1500 GMT (1100 EDT) surface weather chart.
2. The 1600 GMT (1200 EDT) weather depiction chart (nephanalysis).
3. The 1200 GMT (0800 EDT) 850-millibar height analysis.
4. The upper air winds in 1000-foot increments.

In Table 5-2 five numbers per level at each site are given. The first three numbers are the wind direction and the last two are the wind speed in knots. Therefore, the number 25013 means the wind direction is from 250 degrees on a 360 degree circle (north equals 0 and 360) and the wind speed is 13 knots.

If more detailed meteorological data are needed, copies for specific times can be obtained at cost on a limited basis from:

Valentine J. Descamps
Region I Meteorologist
EPA JFK Federal Building
Boston, MA 02203
Telephone number 617-223-5630 (FTS 223-5630)

or

Karl F. Zeller
Staff Meteorologist
EPA, EMSL-LV
Air Quality Branch
P.O. Box 15027
Las Vegas, NV 89114
Telephone number 702-736-2969, x333 (FTS 595-2969, x333)

Table 5-1. METEOROLOGICAL DATA AVAILABLE FOR THE ANALYSIS OF THE NORTHEAST OXIDANT TRANSPORT STUDY

Product	Time measurement	Format
1. Service A surface weather observations (includes: sky conditions, visibility, pressure, temperature, dewpoint, wind direction and speed, altimeter, and comments)	Hourly	Teletype printout (code)
2. Synoptic facsimile maps (weather charts)		Facsimile maps
a. Surface weather chart	3 hour	
b. Weather depiction chart	3 hour	
c. 850-millibar chart (5000 ft MSL)	12 hour	
d. 700-millibar chart (10,000 ft MSL)	12 hour	
e. 500-millibar chart (18,000 ft MSL)	12 hour	
f. Composite radar chart	3 hour	
3. Service C rawinsonde upper air observations for:	12 hour 00-12 GMT[a]	Teletype printout (code)
a. Portland, ME (72606)		
b. Chatham, MA (74494)		
c. Albany, NY (72518)		
d. Fort Totten, NY (74486)		

[a] Limited additional low altitude soundings were taken at 1800 GMT (1400 EDT) at the four rawinsonde stations listed in item 3. The wind direction and speed data are listed in this report. The pressure, temperature and dewpoint data can be obtained from Mr. Karl Zeller.

A separate report on PIBAL observation (upper air winds) collected at Avery Point, Putnam, and West Springfield and low altitude radiosonde observations (temperature and dewpoint lapse rates and upper air winds) collected at the Massachusetts Institute of Technology in Boston (Figure 5-1) was prepared by The Research Corporation (TRC) of New England and is available through the Region I meteorologist.

In addition to the meteorological data, Table 5-3 is included to provide a quick reference to the weather as well as the general location of sampling flights for each of the three participating aircraft per day.

Table 5-2. UPPER AIR WINDS - NORTHEAST OXIDANT STUDY[a]

(Heights in 1000-foot increments)

Date: July 28, 1975

Height	Portland ME	Fort Totten NY	Albany NY	Chatham MA	Avery Point CN	MIT-Boston MA	West Springfield MA	Putnam CN
Time	0800 EDT	0800 EDT	0800 EDT	0800 EDT	0858 EDT	1000 EDT	0900 EDT	0900 EDT
Sfc.	13003	24012	18007	26005				
1		25525	25511	26518	25722		22407	23715
2		28024	28019	27518	27329	26315	28019	
3		25019	29020	28521		27313	29017	
4		26518	29522	29023		25620	29118	
5				26522		25354	28220	
6	27522	26518	28022	26521			27822	
7	27023	26521	27521	27020			27229	
8	27025	26026	28022	27021			26128	
9	26524	26031	27524	27021			25328	
10								
12	25026	26039	25530	27027				
Time	1400 EDT	1400 EDT	1400 EDT	1400 EDT	1450 EDT	1350 EDT	1500 EDT	1500 EDT
Sfc.		28004		20022				
1		28507		22032	24617	05910	27119	24707
2		29508		23035	27217		26812	23710
3		28509		23534	29315		25410	24112
4		28510		24033	30317		22406	25713
5		28510		23532			24808	26617
6		26512		23529			25212	
7		25517		24531			25517	
8		25520		25031				
9		26023		25033				
10		26525		24532				
12		26531		23533				
Time	2000 EDT	2000 EDT	2000 EDT	2000 EDT		1501 EDT		
Sfc.	19008	18007		21022				
1	23524	34004		23031		09408		
2	24025	35011		23528		07409		
3	24524	28513		23526				
4	24523	28511		24525				
5	24023	28012	25017	25027				
6	24022	27014		25029				
7	24021	25019		24531				
8	25520	25521		24530				
9	25520	25022		24029				
10	25521	26027	26524	24530				
12	25014	26529		24034				

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[a] The first three numbers indicate wind direction in degrees; the last two, wind speed in knots.

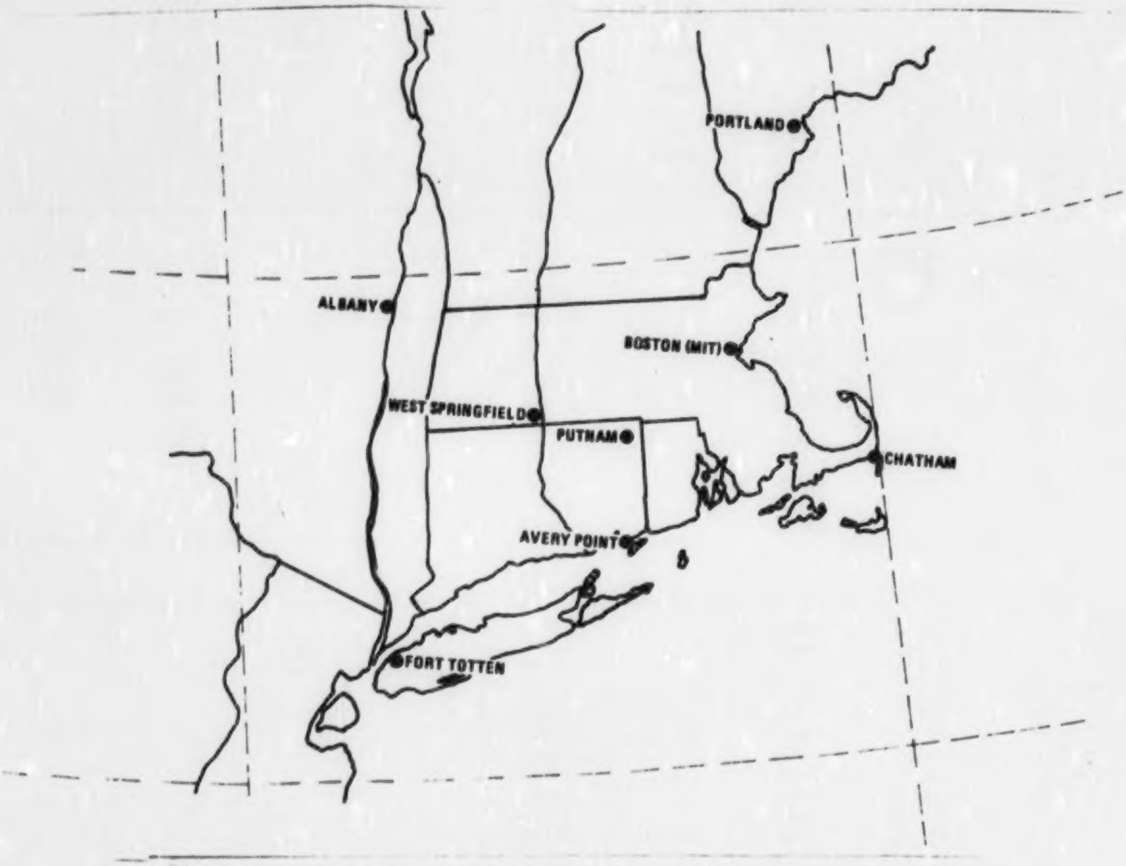

PORTLAND
ALBANY
BOSTON (MIT)
WEST SPRINGFIELD
PUTNAM
CHATHAM
AVERY POINT
FORT TOTTEN

Figure 5-1. Geographic location of rawinsonde and PIBAL stations.

Table 5-3. FLIGHT LOCATIONS AND METEOROLOGY

Date	Battelle flight	Washington State University flight	Surface synoptic situation over southern Region I	850-mb flow (12Zℓ)
7/15		p.m.--Long Island Sound	Weak front N-S in West of Region; SCTD to BRKN clouds over entire area; high pressure ridge moving in from east	SSW, 30K
7/18	Evening--normal	Early p.m.--spiral at mouth of Connecticut late p.m.--East Connecticut	High pressure ridge south of Region; SW surface flow OVC eastern portion of Region	SW, 15K
7/19		a.m.--Long Island Sound & West Connecticut p.m.--normal (old)	Same as 18th; clouds SCTD to BRKN over entire Region	SW, 25K
7/20		p.m.--Long Island Sound	Cold front to NW moving E; surface flow S thru SW; OVC over most of Region	SW, 30K
7/21	Evening--normal	a.m. - p.m.--normal p.m.--Long Island Sound-Conn. R.	Cold front just off Region coast; surface flow W; SCTD clouds over region	Trof over region, NW thru W, 20K
7/22	a.m.--Long Island-NYC p.m.--Long Island-NYC	a.m.--Long Island Sound p.m.--Long Island Sound	High pressure center over Ohio; surface flow mixed; SCTD clouds over Region	W thru SW, 20K
7/23	a.m.--normal p.m.--normal	a.m.--normal p.m.--Long Island Sound & W. Conn.	High centered over Maryland; cold front to NW moving E; surface flow SW; clouds SCTD to BRKN over Region	WNW, 20K
7/24	p.m.--Atlantic Ocean (downwind Boston)	a.m.--normal p.m.--normal	Low centered to NW with frontal system moving E; surface flow S thru SW, clouds BRKN to OVC over Region	SW, 20K
7/25			Cold front N-S on west boundary of Region I moving E; surface flow SW; OVC over Region	
7/26	a.m.--normal p.m.--normal	a.m.--normal p.m.--normal	High pressure centered over Ohio; surface flow NW thru W; SCTD clouds over Region	NW thru W, 20K
7/27	a.m.--normal p.m.--normal	a.m.--normal p.m.--normal	Cold front to W; hurricane to SE; surface flow E; SCTD clouds over Region	VRBL, 5K
7/28	a.m.--Hudson River of normal	a.m.--LI Sound p.m.--LI Sound	Cold front N-S in center of Region moving E; surface flow SW to E of front, W behind; clouds SCTD to BRKN over Region	W, 20K
7/29	a.m.--normal (cw) p.m.--normal (cw)	a.m.--normal p.m.--normal	High pressure centered over West New York; surface flow NW; skies CLR to SCTD	W, 20K
7/30		Night south of Boston	High pressure over E Penn.; surface flow W; skies CLR	NNW, 10K

Table 5-3 (continued). FLIGHT LOCATIONS AND METEOROLOGY

Date	Battelle flight	Washington State University flight	Surface synoptic situation over southern Region I	850-mb flow (12Z)
7/31			High pressure center over SW Penn.; surface flow W; clouds BRKN.	
8/1			High pressure centered over W Penn.; trof off Mass. coast; surface flow VRBL, 5K; SKTD to BRKN clouds	NE, 20K
8/2		p.m.--South of Boston-Cape Cod night–South of Boston-Cape Cod	High pressure ridge S-N W of Region I; surface flow VRBL, 5K; clear skies	N thru NE, 20K
8/3	Return to Ohio	Noon--normal	Back door cold front N-S thru center of Region I; surface flow VRBL, 10K; clouds BRKN to OVC	NW, 5K
8/4	Rain	Rain	Small high pressure ridge N-S, E of Region I; surface flow E, 10K; clouds BRKN to OVC over Region I	SW, 10K
8/5	a.m.--plume tracking (power plant)	p.m.--LI Sound	Occluded front N-E E of Region; cold front N-S of Region; surface flow VRBL, 5K; clouds SCTD over Region	NW, 10K
8/6	a.m.–New York City	a.m.--downwind-Boston p.m.--downwind-Boston		

6. OZONE AND OTHER POLLUTANTS MEASURED BY THE ENVIRONMENTAL PROTECTION AGENCY, LAS VEGAS, DURING THE 1975 NORTHEAST OXIDANT TRANSPORT STUDY

George W. Siple
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Las Vegas, NV

The participation of the Environmental Monitoring and Support Laboratory at Las Vegas in the Northeast Oxidant Transport Study was a two-fold measure. First, we provide a field meteorologist, Mr. Karl Zeller, who was responsible for day-to-day coordination of the various airborne monitoring teams. Second, we gathered extensive air quality data utilizing the Long Range Air Monitoring Aircraft (LORAMA), often referred to as the B-26. This paper deals with the operational capabilities of the LORAMA and its application in the study during the summer of 1975.

First is a discussion of the system of instrumentation on board the aircraft. For the purpose of this study, we monitored a number of pollutant and meteorological parameters. During each flight, ozone was measured by the gas-phase chemiluminescent Bendix 8002, which has proven to be a stable and precise ozone analyzer. In addition to the Bendix analyzer, a Dasibi 1003-AAS, based on the absorption of light by ozone, was on line during several of the later flights to aid in evaluating the equivalency of the two methods under field conditions. Nitric oxide was measured on a single-channel TECO 14B gas-phase chemiluminescent analyzer, modified for high sensitivity. This particular instrument is designed to reliably measure oxides of nitrogen in the range of 0 to 5 ppb, full scale. Temperature, dewpoint, altitude, and position were automatically recorded on a routine basis. Grab bag samples were taken on most days, at strategic points in the flight patterns: mainly in regions of elevated ozone values. An MRI integrating nephelometer was installed to measure particulate matter according to its light scattering properties. The nephelometer is provided with a heating element that reduces the moisture content of the sample air when the flow rate is approximately 10 to 15 cfm. The installation of the nephelometer in the EPA-LV aircraft is designed for ram air to flow through the instrument, providing a flow rate as much as ten times that which affords optimum operation of the air drying mechanism. This vitiates the effectiveness of the heater; that is, the heater is unable to sufficiently dry the sample air entering the nephelometer. For that reason, the reported values essentially correspond to "wet bscat."

Prior to the study, both the Bendix 8002 and the TECO 14B were tested for stability under conditions of changing temperature and pressure, simulated in an environmental chamber at the Las Vegas lab. These tests sought to isolate the degree of baseline shift and gain shift corresponding to the changing ambience of an unpressurized aircraft. Under conditions of changing temperature at constant pressure, the only notable result was the zero level shift of the TECO. Under conditions of changing pressure at constant temperature, the notable results concern the span shift of both the Bendix and TECO.

In the field, calibration was performed on all instruments before and after each day's flights, checking both zero and span levels. During each flight, periodic zero level checks were also performed. These calibration data, along with the correction factors derived from the environmental chamber tests, were incorporated into the program used to process the data from the raw voltage values into the reported engineering units. We now have the system capabilities for the LORAMA field team to process data within 24 hours of collection, i.e., while still in the field. This is a great advantage for quality control considerations and for rapid initiation of data interpretation. A copy of this process data has been presented to EPA Region I and a copy to Joe Bufalini of EPA, Research Triangle Park, NC.

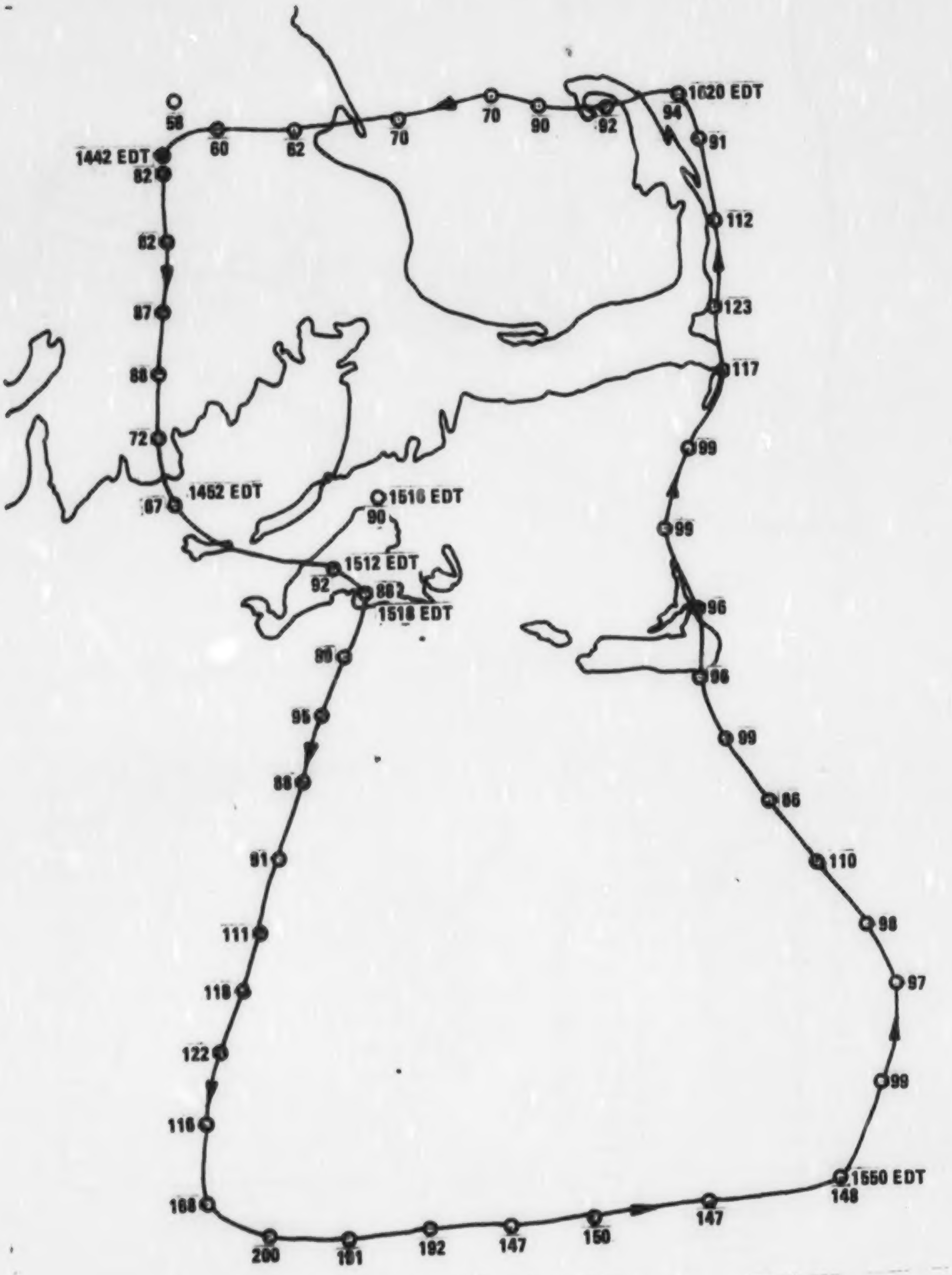
After the data were processed, they were reduced into visual representations to aid in the analysis. This has taken two general forms, and I would like to illustrate examples of both kinds. First, are the spatial ozone distribution maps constructed from flights made during the study. Figures 6-1 and 6-2 are two examples of flight patterns flown by the B-26. In these flights, the area of principle concern was that west of New York and south of Boston. These maps show time of day and instantaneous ozone values. The instantaneous values are good approximations of longer-term averages, except where values are rapidly changing.

The second type of visual representation is the vertical profile made for each pollutant and meteorological parameter measured by the B-26 aircraft. Examples of these types of measurements are given in Figure 6-3. These types of data representations can be produced while still in the field, within a day of the data collection time.

Finally, here are a few comments on our quality assurance program. Figure 6-4 shows the traceability of the ozone calibration standard from the Federal Register standard calibration reference method to the field monitor. Because of its stability, the Dasibi instrument was chosen to transfer this standard to the Bendix analyzer.

As I mentioned before, a calibration was performed daily, after each flight and before the next. A Bendix 8851-X Dynamic Calibration System was used to generate ozone for span calibration. The Dasibi was used to measure this span value and also to check the quality of the zero air. The Bendix ozone analyzer has been shown to be a stable instrument. However, experience has shown it to be good practice to calibrate frequently, especially when the instrument is subject to a stressful aircraft environment, to minimize spurious data.

On August 12, all three aircraft participated in a concomitant flight. Review of the data indicates that the LORAMA ozone data are approximately 15 percent lower, on the average, than those ozone values measured by the other aircraft. At this time, we have not isolated the reason for this discrepancy, but we are looking into it further.



58
1442 EDT
60
62
70
70
90
92
94
1620 EDT
91
82
82
87
88
72
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1516 EDT
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1512 EDT
92
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1518 EDT
112
123
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99
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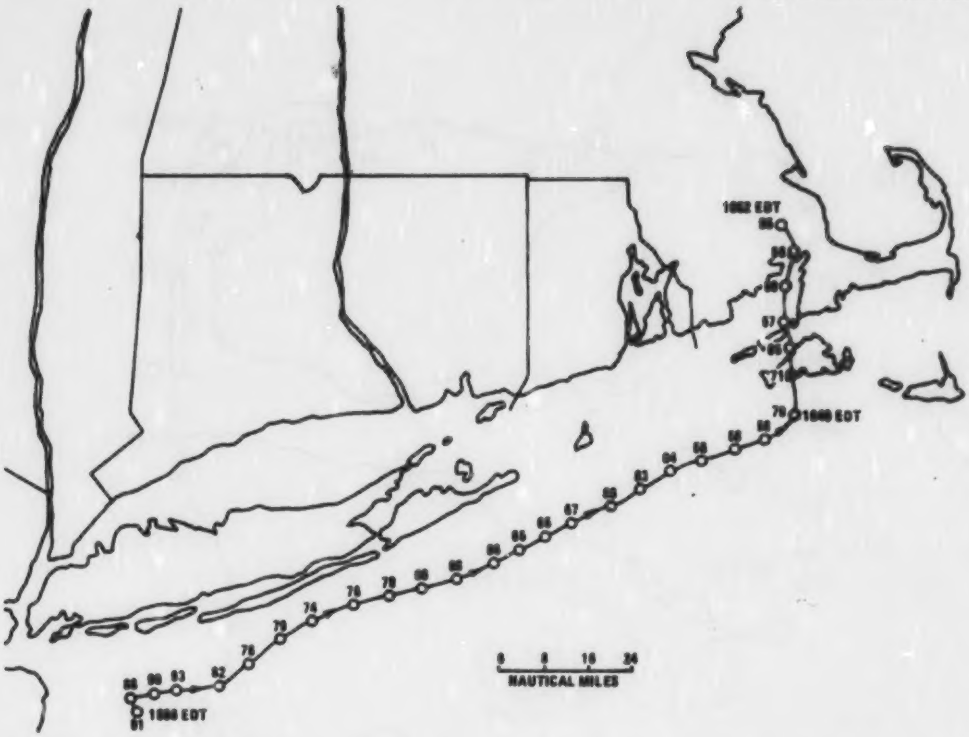
98
97
99
1550 EDT
148
89
95
88
91
111
118
122
116
168
200
191
192
147
150
147

Figure 6-1. Flight pattern and ozone results (in ppb) for afternoon flight of August 14, 1975.


EDT
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74
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NAUTICAL MILES

Figure 6-2. Flight pattern and ozone results (in ppb) for afternoon flight of August 27, 1975.

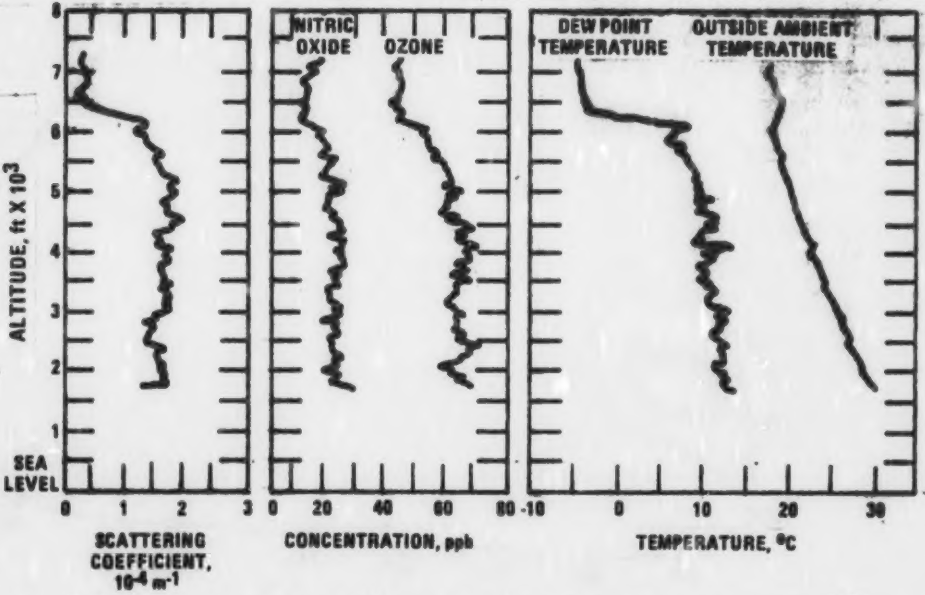

Figure 6-3. Vertical profiles of various pollutant and meteorological variables measured by the B-26 aircraft.

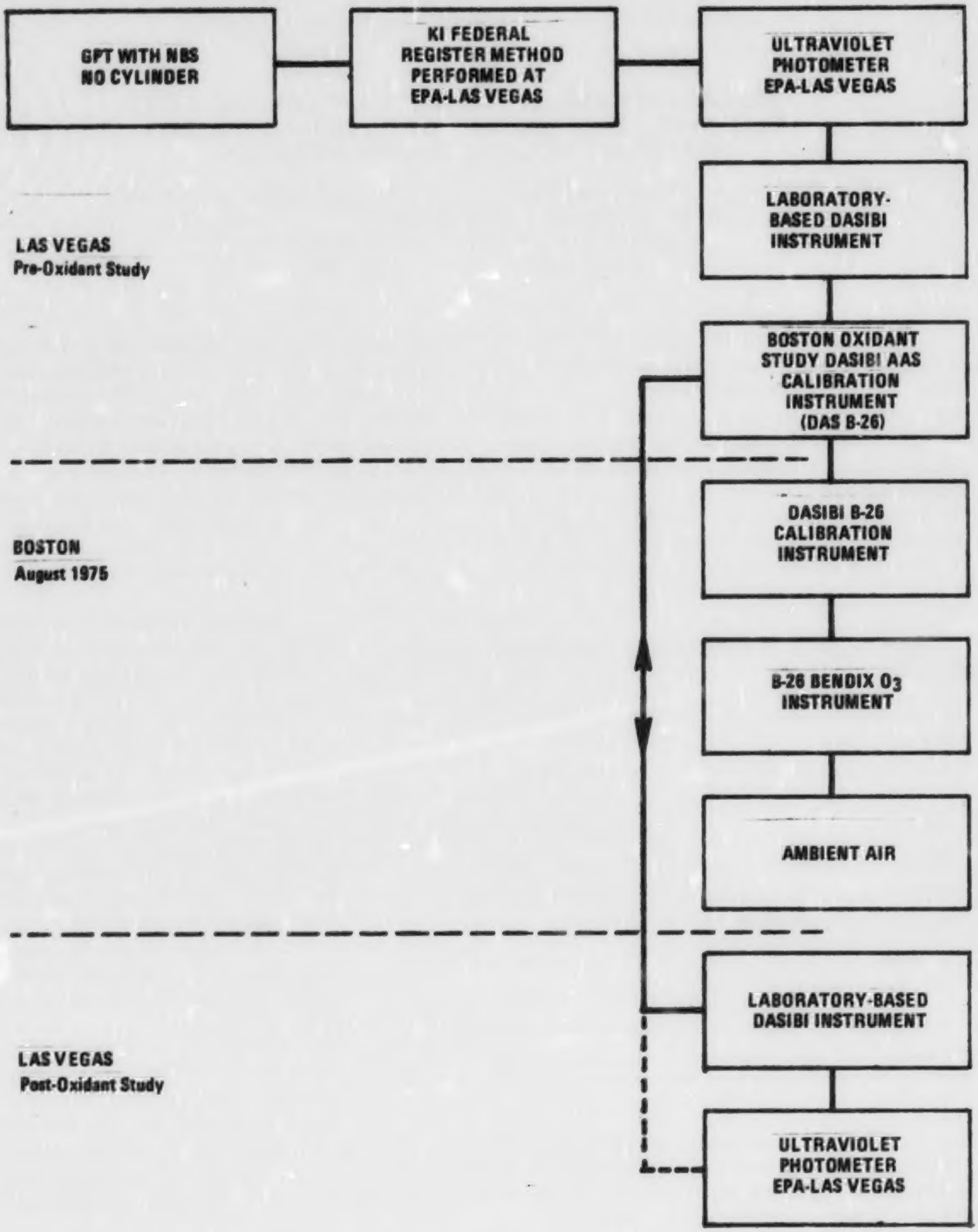
GPT WITH NBS NO CYLINDER
KI FEDERAL REGISTER METHOD PERFORMED AT EPA-LAS VEGAS
ULTRAVIOLET PHOTOMETER EPA-LAS VEGAS
LABORATORY-BASED DASIBI INSTRUMENT
LAS VEGAS
Pre-Oxidant Study
BOSTON OXIDANT STUDY DASIBI AAS CALIBRATION INSTRUMENT (DAS B-26)
BOSTON
August 1975
DASIBI B-26 CALIBRATION INSTRUMENT
B-26 BENDIX O3 INSTRUMENT
AMBIENT AIR
LABORATORY-BASED DASIBI INSTRUMENT
LAS VEGAS
Post-Oxidant Study
ULTRAVIOLET PHOTOMETER EPA-LAS VEGAS

Figure 6-4. EPA - Las Vegas field calibration scheme.

7. PRELIMINARY RESULTS OF HYDROCARBON AND OTHER POLLUTANT MEASUREMENTS TAKEN DURING THE 1975 NORTHEAST OXIDANT TRANSPORT STUDY

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The location of the EPA-RTP mobile laboratory during the 1975 Northeast Study was at Chickatawbut Hill (elevation 517 feet) located in the Blue Hills reservation near Quincy, approximately 10 miles south of downtown Boston, MA. The laboratory was fully equipped to continuously measure many gaseous pollutant concentrations as well as several meteorological variables. The equipment array is listed in Table 7-1. In addition to these continuous measurements, C_1-C_{10} hydrocarbon compositional determinations were made by gas chromatographic procedures[1] for bag samples collected by aircraft and at selected ground sites. The aircraft bag samples analyzed were primarily those collected by the EPA-LV B-26 aircraft; however, on occasion, some aircraft samples collected by Washington State University and Battelle were analyzed.

Ground samples were collected at four ground sites including the Chickatawbut location. For these studies, 2- and 3-hour integrated bag samples were collected with an automated sampler at two sites simultaneously over a 24-hour period. The other ground sites included the 25th floor of J.F.K. Federal Building in downtown Boston, the second floor of the science building on the campus of the Essex County Industrial Farm in Danvers, MA, approximately 25 miles northeast of downtown Boston, and a penthouse room at the Massachusetts State Mental Hospital in Medfield, MA, approximately 25 miles southwest of downtown Boston. Ozone measurements were also made at each of these sites during the field study sample period. Ground samples were also collected in the Sumner and Callahan tunnels and along downtown highway locations in an effort to determine auto exhaust composition and hydrocarbon to acetylene ratios.

Table 7-1. MOBILE LABORATORY INSTRUMENT ARRAY

Pollutant	Instrument
Nitrogen oxides	TECO 14B
Total hydrocarbon, methane, carbon monoxide	Beckman 6800
Total sulfur	Meloy SA-120
Ozone	Bendix model 8002
PAN	G.C.-electron capture
Freon-11, carbon tetrachloride	G.C.-electron capture
Visibility	MRI-integrating nepholometer
UV-visible radiation	Eppley radiometer
Wind speed and direction	Bendix aerovane system
Temperature - relative humidity	Hydrothermograph

The study period commenced on July 17 and extended to August 29, 1975. The following tables and figures of data are intended to represent some of the preliminary findings of this study.

Table 7-2 represents the average percentage composition of the total hydrocarbons for the sum of the identified olefins, paraffins, and aromatic compounds for the bag samples collected during the 600 to 900 and 1500 to 1800 time periods at each of the ground sites. The average percentage acetylene of the total hydrocarbon is also included. The JFK data were excluded from this comparison since paint vapor contaminates of the heavy molecular weight hydrocarbon variety dominated the composition.

Although this percentage representation has limited usefulness, three observations can be made:

1. The general consistency in the composition between the three ground sites.
2. Sources of hydrocarbon other than vehicular tailpipe emissions at the ground sites are evident by the lower percentage of acetylene compared to the tunnel samples. These other hydrocarbons are obviously paraffins and aromatics.
3. Some photochemical loss of the olefinic hydrocarbons is suggested at both sample time intervals. This is concluded by the comparison of the ratio of the percent of sum of olefins to percent of acetylene between the ground and tunnel sites.

Table 7-2. COMPARISON OF HYDROCARBON COMPOSITION AT GREATER BOSTON AREA GROUND SITES TO ROADWAY AND TUNNEL SAMPLES, 1975
(percent)

	Tunnel and roadway	Chickatawbut	Danvers	Medfield
0600-0900 hours				
Paraffins	48	52	58	58
Olefins	20	09	09	09
Aromatics	32	39	33	33
Acetylene	5.1	3.1	3.1	3.6
1500-1800 hours				
Paraffins	48	63	50	50
Olefins	20	08	07	10
Aromatics	32	29	43	40
Acetylene	5.1	2.7	3.3	2.6

Figure 7-1 represents the diurnal variation of the sums of olefins, paraffins, and aromatics for July 18, 1975. It is apparent that sources other than tailpipe emissions contribute to the total hydrocarbon burden by the inconsistency between the diurnal patterns. During the 0300 to 1000 time period, other paraffin sources are evident, primarily at the expense of the sum of aromatics. This trend reverses during the 1000 to 1700 period. The composition becomes consistent for the remaining time periods. The olefin composition is fairly consistent throughout the day, with some indication of olefin loss during the 0900 to 1500 time period.

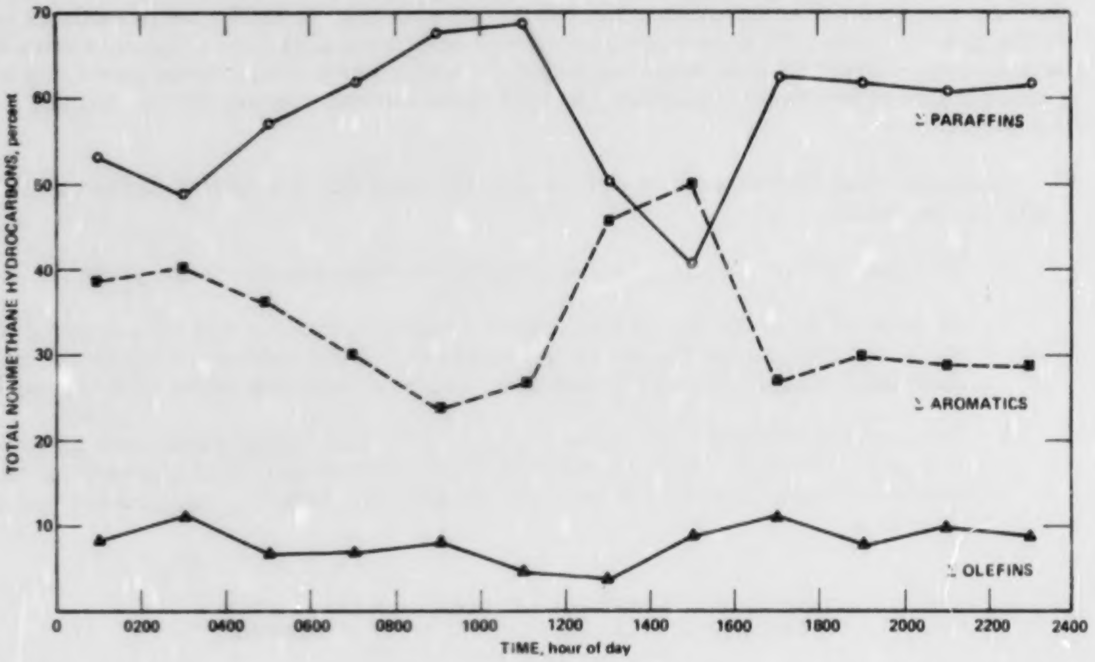

Figure 7-1. Diurnal variation of Σ paraffins, Σ aromatics, and Σ olefins as percentage of total nonmethane hydrocarbons, Chickatawbut Hill, July 18, 1975.

Some natural hydrocarbons of the terpene variety have been observed to elude from our gas chromatograph columns at retention times similar to peaks identified as vehicular type hydrocarbons. Two such examples are shown in Figure 7-2. In the top figure, diurnal patterns of 1,2,4-trimethylbenzene and m- and p-ethyltoluene are plotted. In the tunnel and roadway samples, these two peaks were generally at equal concentrations; however, this is not the case at the Chickatawbut site for this particular day's study. It appears that other sources of either 1,2,4-trimethylbenzene or another compound occur during each sample period, especially during the 1100 to 1700 and 1700 to 2100 time periods. In previous studies, d-limonene was found to have a similar retention time to 1,2,4-trimethylbenzene. It is merely speculative to assume that the difference between these two curves is d-limonene, since the half life of this compound in the presence of 100 ppb ozone is approximately 3 minutes; however, it is doubtful that this peak is entirely 1,2,4-trimethylbenzene.

Another similar example is presented in the lower plot of Figure 7-2. In the tunnel and roadway samples, a consistent 3 to 1 ratio was observed for the ratio of carbon concentration of 2-methylpentane to cyclopentane. This ratio was observed at the Chickatawbut Hill site in the early morning hours; however, during the 0800 through 2300 time period, the cyclopentane peak becomes the more abundant peak. During the afternoon, this peak is approximately 30 ppb carbon larger than expected. The only identified compound with a similar retention time to cyclopentane is isoprene. The general area at the Chickatawbut Hill site is surrounded by woodland vegetation, which may explain these unusual peak ratios. Red Oak trees are common to the area and are known emitters of isoprene, especially during daylight hours. The ozone levels during these afternoon hours exceeded 100 ppb.

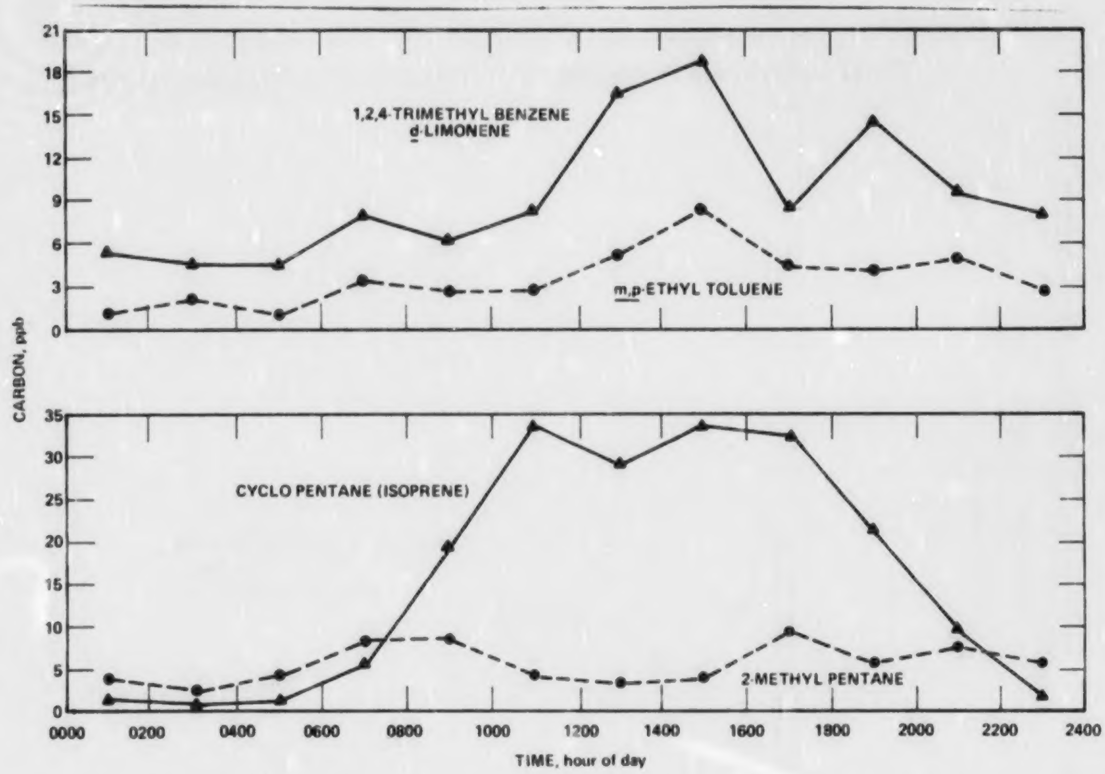

Figure 7-2. Diurnal variation of hydrocarbon compounds, Chickatawbut Hill, July 18, 1975.

The mercuric sulfate-sulfuric acid scrubber technique was used on other samples exhibiting unusually high cyclopentane concentrations and confirmed that most of the peak area was olefinic. The use of this scrubber technique on the 1,2,4-trimethylbenzene peak were inconclusive.

In recent years, field studies were conducted in rural atmospheres of low hydrocarbon concentrations. During these studies, bag surface out-gassing contamination was observed in many of the analyzed bag samples. In an effort to investigate the outgassing nature of the Tedlar polyvinyl fluoride film, a series of experiments were performed to evaluate temperature and sunlight irradiation effects.[2]

The results of a 6-hour exposure of simulated sunlight on a Tedlar bag containing zero hydrocarbon grade air are given in Figure 7-3. Several peaks that would interfere with the accurate analysis of stored ambient air samples were observed on the silica gel and dibutylmaleate columns. Interfering peaks occurred to a smaller extent on the aromatics column.

Outgassing as a function of increased temperature was investigated by placing a Tedlar bag filled with zero hydrocarbon grade air in a large drying oven at 50°C for several hours. A temperature of 50°C (122°F) was chosen as a maximum expected ambient air temperature.

It was observed that increased temperature resulted in little or no significant peak interference on the silica gel or dibutylmaleate columns; however, similar peaks

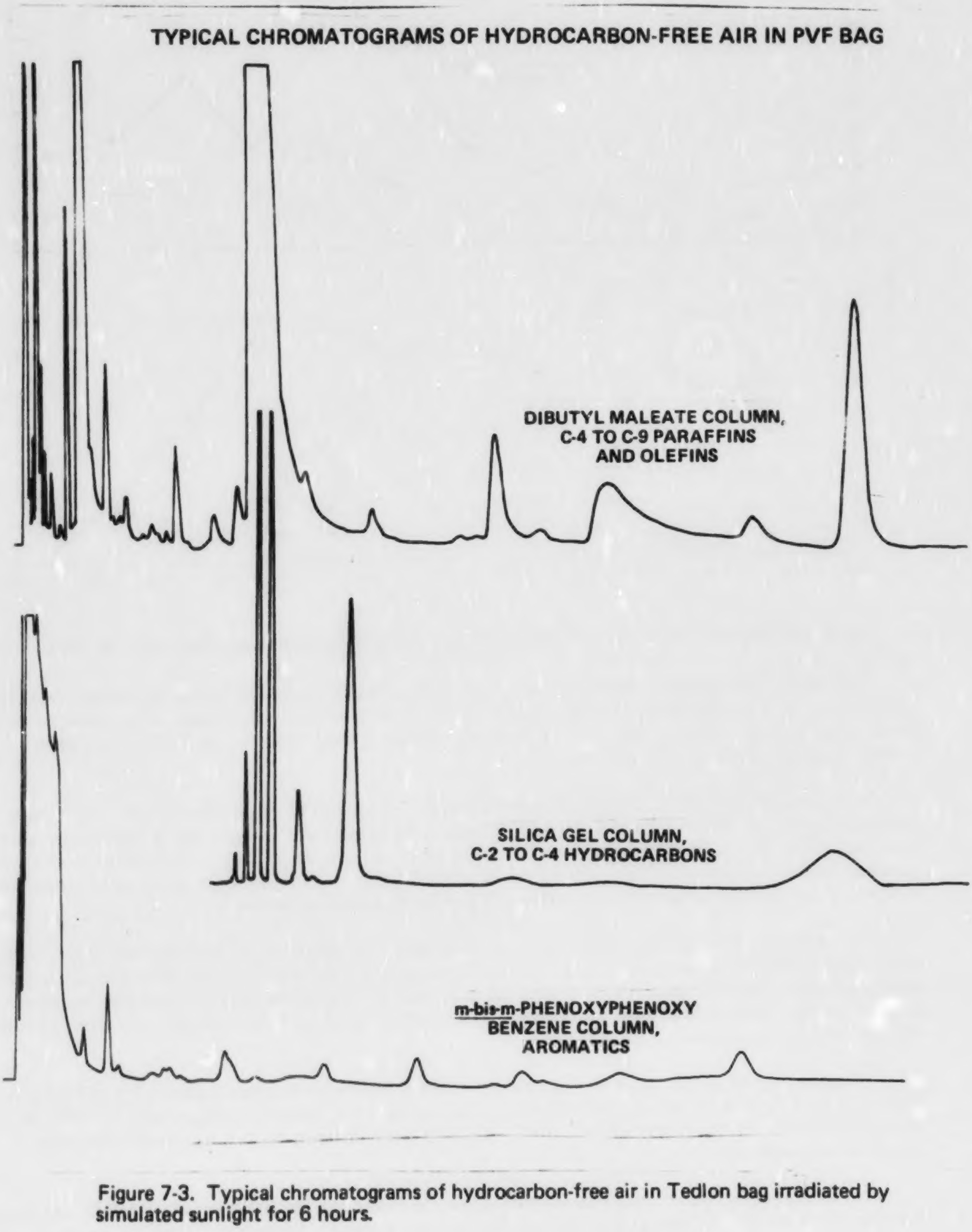

Figure 7-3. Typical chromatograms of hydrocarbon-free air in Tedlon bag irradiated by simulated sunlight for 6 hours.

observed during the irradiation studies on the aromatics column were observed during these studies but at significantly higher concentrations. In fact, the last peak on the aromatics chromatograph was identified as dimethylacetamide, the solvent used in the extrusion process for making Tedlar film.

It was concluded from these studies that the outgassing peaks observed on the silica gel and dibutylmaleate columns were the result of photochemical degradation, whereas, the peaks observed on the aromatics column were the result of temperature desorption. It was also concluded that Tedlar bags could be used for these studies as long as they were covered with black polyethylene to block out sunlight and stored at reasonable ambient temperatures.

Representative diurnal patterns of ozone and other pollutions at the Chickatawbut Hill site are given in Figures 7-4 to 7-7. Figures 7-4 and 7-5 represent those days in which double ozone peaks were observed during the 24-hour sampling period. The first ozone peak occurs during the early afternoon hours and could be representative of the photochemistry of local area emissions. This contention is somewhat indicated by the typical early morning buildup of vehicular emissions observed by the increase in acetylene during the 0600 to 0900 time period (Figure 7-4) and the 0800 to 1000 increase of carbon monoxide (Figure 7-5).

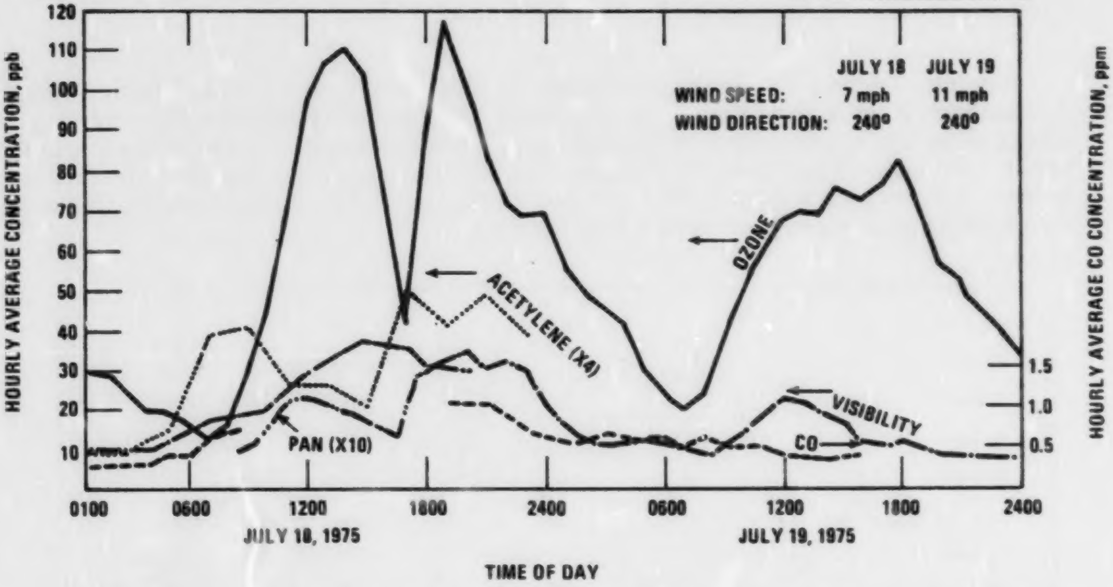

Figure 7-4. Diurnal hourly concentrations of ozone, carbon monoxide, acetylene, and visibility, Chickatawbut Hill, July 18 and 19, 1975.

The second ozone peak appears during the late evening hours and was obviously the result of transported ozone from southwest locations in the case of Figure 7-4 and from west to northwest locations in the case of Figure 7-5. The geographical origin of this ozone is difficult to predict, but from ground wind speed considerations, the distance was probably 50 to 100 miles. This distance would be longer if one also considered early morning ozone precursor transport. In Figure 7-4, corresponding increases of acetylene and PAN during the nighttime ozone peak indicate its anthropogenic origin.

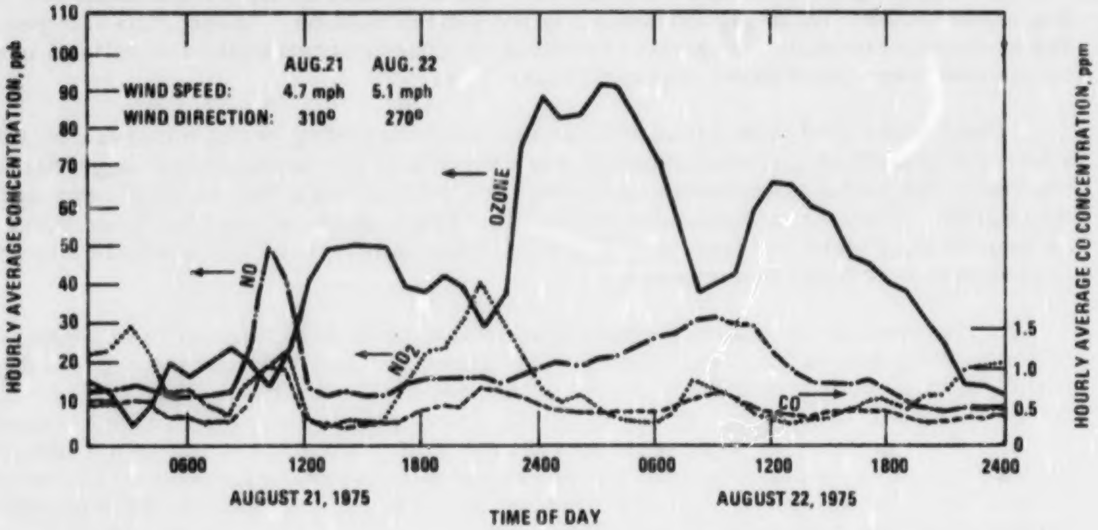

Figure 7-5. Diurnal hourly average concentrations of ozone, nitric oxide, nitrogen dioxide, and carbon monoxide, Chickatawbut Hill, August 21 and 22, 1975.

Figures 7-6 and 7-7 represent diurnal patterns of ozone that starts to build up to maximum during the early afternoon hours and persists into the late evening. These days are representative of high ozone levels persistent over large regional areas. On both of these days, the ozone maximum occurs during the late evening hours. Corresponding PAN data of July 28 (Figure 7-6) demonstrate that both photochemical products were of tropospheric origin.

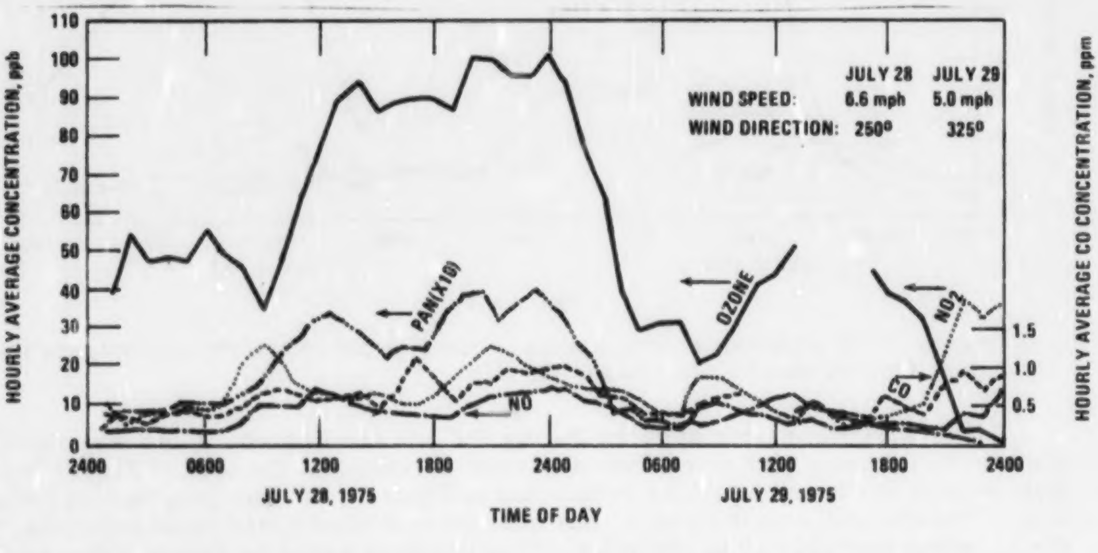

Figure 7-6. Diurnal hourly average concentrations of ozone, nitric oxide, nitrogen dioxide, and carbon monoxide, Chickatawbut Hill, July 28 and 29, 1975.

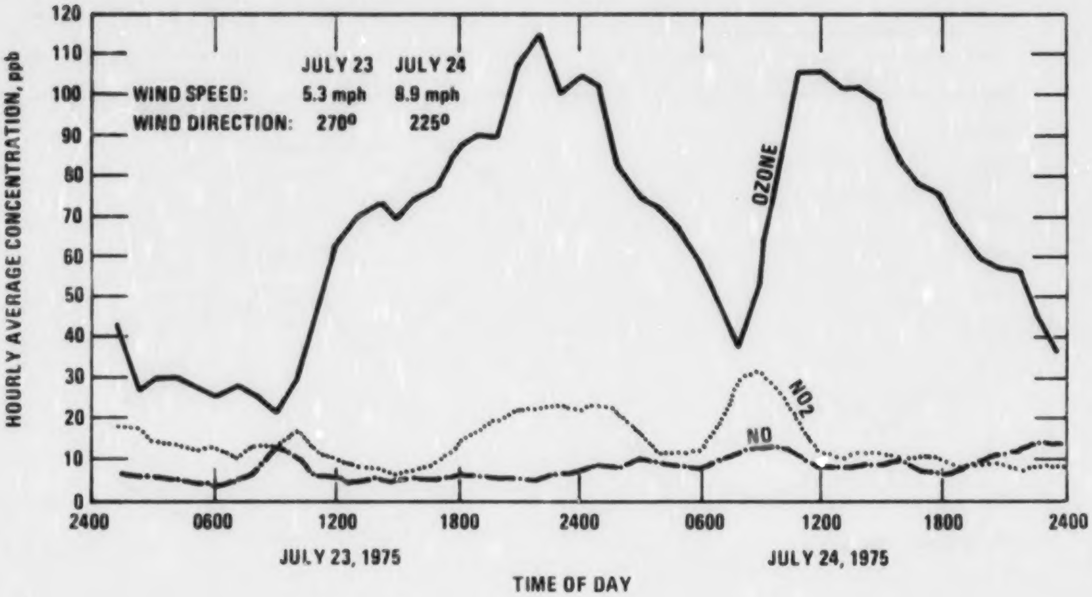

Figure 7-7. Diurnal hourly average concentrations of ozone, nitric oxide, and nitrogen dioxide, Chickatawbut Hill, July 23 and 24, 1975.

Figure 7-8 and 7-9 represent comparison plots of ozone and carbon monoxide for the Chickatawbut Hill and J.F.K. Federal Building sites. In effect, the plots represent ozone patterns of urban and suburban ozones. Figure 7-8 in particular represents what has typically been described as the so-called "urban effect"; that is, the suppression of ozone by fresh emissions of nitric oxide from vehicular sources. Higher vehicular emissions at the urban site are obvious by the comparison of the carbon monoxide patterns. The tendency of fresh vehicular sources is to suppress ozone in the urban areas and produce high ozone concentrations downwind of the urban complex. In Figure 7-9, the ozone maximum at the J.F.K. site is approximately the same magnitude as that observed at the Chickatawbut Hill site; however, it occurs later in the afternoon and was probably the result of a transported air mass.

Figure 7-10 represents the frequency distribution of time versus high hourly average ozone concentrations at the Chickatawbut Hill site. High ozone concentration is defined as 80 ppb or higher. There were a total of 99 high hourly average ozone concentrations observed during this study, which represented 8.8 percent of all of the hourly average measurements made. This 8.8 percent is lower than the 13 to 14 percent observed at the various rural sites during the 1974 Midwest study[3] and considerably lower than the 20 to 30 percent observed during the 1973 Midwest study.[4] Since all three of these studies were conducted during similar summertime seasons, the differences were probably due to meteorological variations. Although the data are not presented here for comparison, the high pressure systems moving through the northeast were faster and less stable than the highs moving through the midwest during the 1973 and 1974 seasons.

Approximately 29 percent of the high ozone averages were observed during the nighttime hours from 0000 to 0500 and 1900 to 2400. Since the formation of ozone from photochemical processes is for all purposes zero during these time intervals, these high ozone levels were the result of transported air masses.

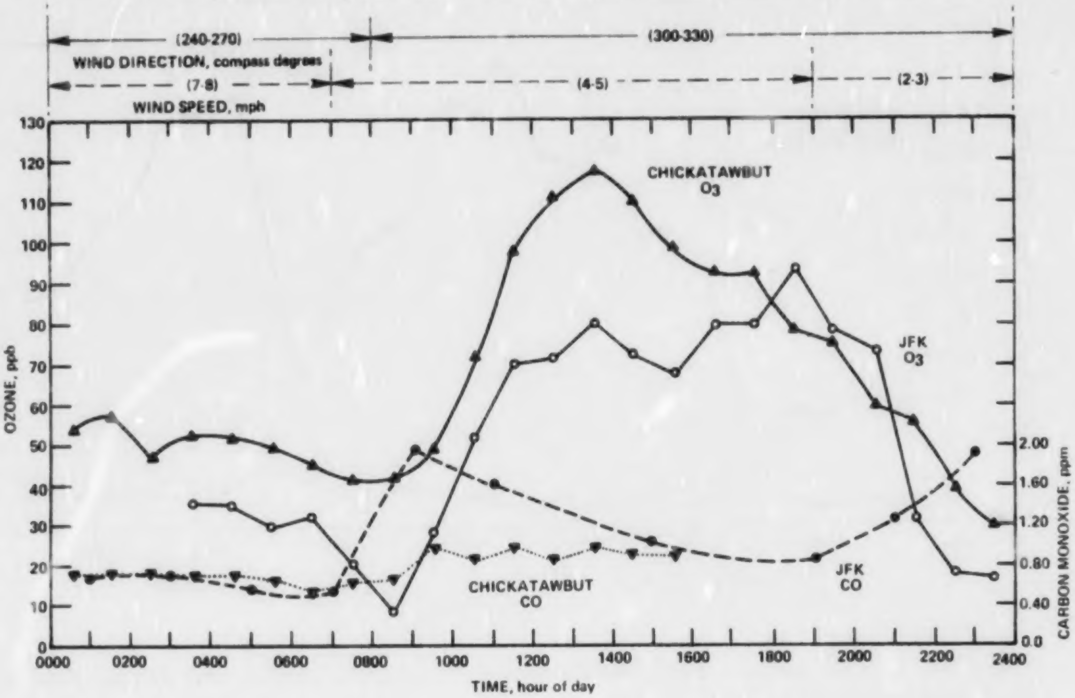

Figure 7-8. Comparison of JFK Building with Chickatawbut Hill, July 31, 1975.

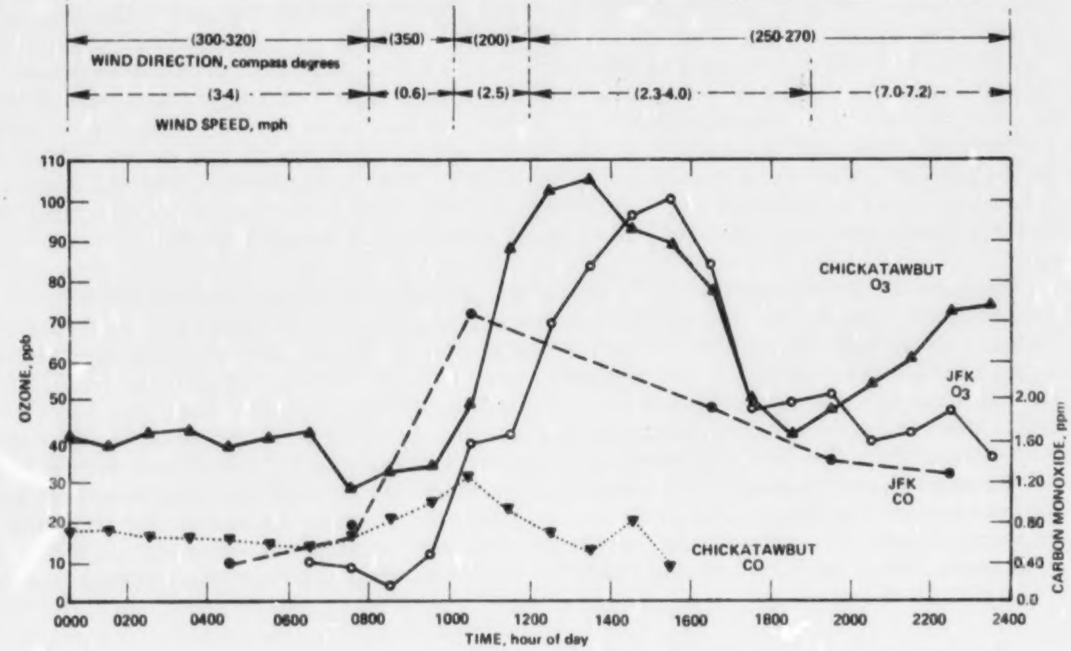

Figure 7-9. Comparison of JFK Building with Chickatawbut Hill, August 11, 1975.

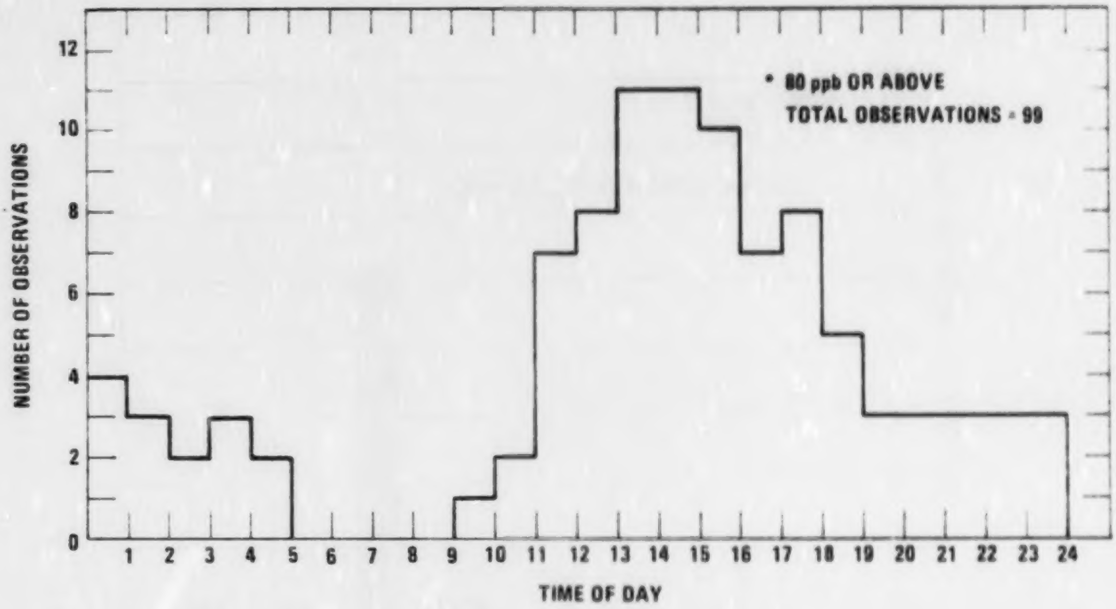

Figure 7-10. Frequency distribution of time versus high * hourly average ozone concentrations.

Approximately 13 percent of these high ozone hourly averages occurred on weekends; that is, Saturday and Sunday. Since weekend days represent 26 percent of the total week period, one can conclude that the so-called "week-end effect" was not observed at this site during the study period. The "weekend effect" is described as higher weekend ozone concentrations than week days due to higher HC/NO_x ratios and more favorable NO_2/NO ratios for earlier ozone formation. The J.F.K. sites, or in general urban sites, are more likely candidates to demonstrate "weekend effects"; however, these data have not yet been analyzed.

Figure 7-11 represents the frequency distribution of wind direction versus high hourly average ozone levels. The nighttime or darkened areas represent the time periods of 1700 to 2400 and 0000 to 0500. It is obvious that most of the high hourly average ozone concentrations were observed when the winds were generally from the west, in particular the southwest. Practically all (90 percent) of the nighttime high hourly average ozone observations occurred when the winds were from the southwest.

Table 7-3 represents some of the detailed hydrocarbon and corresponding ozone data collected by the EPA-Las Vegas aircraft during the study period. Included in the table are ranges of various results for all the flights during the study period as well as the range of various data for the flight when both the highest and lowest ozone were observed. The August 28 flight was performed to measure background levels for ozone and hydrocarbons in the area of Eastport, ME. There has been some interest in the construction of a petroleum refinery in this general area. It can be seen from the table that most of the low hydrocarbon and ozone measurements observed during the entire study were made during this particular flight. Occasionally high concentrations of ethane and propane were observed in some of these samples, even though the methane concentrations were not unusually high. The origin of these high concentrations are difficult to explain, although the only two known sources are either natural gas leaks or geological emissions from oil fields. The aromatic and

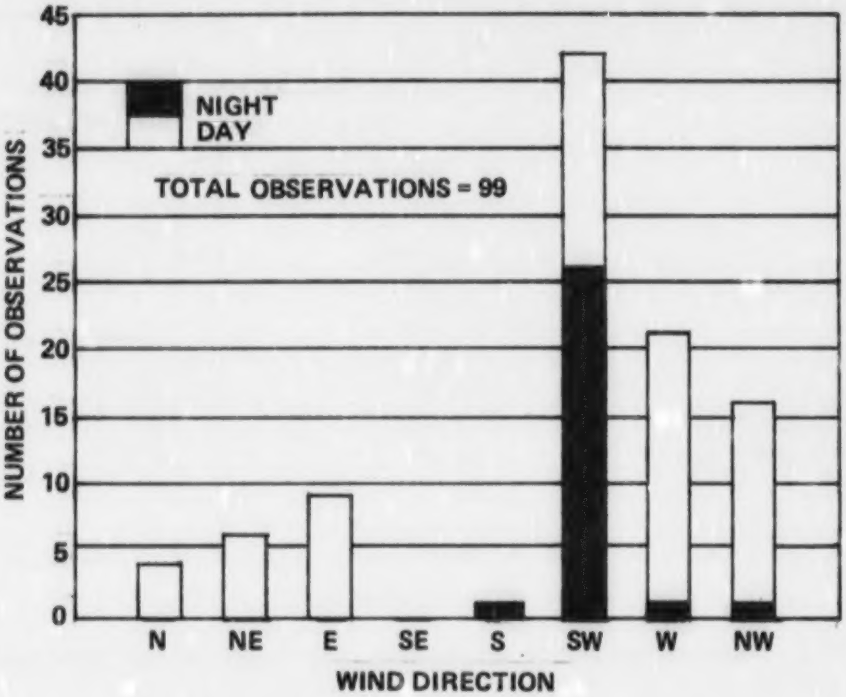

Figure 7-11. Frequency distribution of wind direction at times of high ozone levels.

Table 7-3. AIRCRAFT SAMPLES TAKEN AUGUST 11-28, 1975 - BOSTON OXIDANT STUDY (RANGE OF OBSERVATIONS)

	August 14	August 28	All samples
Acetylene, ppbC	1.0 - 7.1	0.2 - 0.5	0.2 - 7.1
Sum of paraffins, ppbC	17.3 - 84.1	8.9 - 195.7	8.6 - 244.2
Sum of olefins, ppbC	4.4 - 11.6	0.3 - 9.0	0.3 - 14.5
Sum of aromatics, ppbC	23.3 - 47.7	5.4 - 13.7	5.4 - 53.2
Sum of NMHC, ppbC	53.1 - 195.0	17.0 - 211.2	17.0 - 267.7
Ethane + propane, ppbC	10.5 - 47.9	3.9 - 164.7	2.5 - 164.7
Ozone, ppb	53 - 186	27 - 30	27 - 186

paraffinic hydrocarbons represent, as expected, the largest fractions of total nonmethane hydrocarbon.

Table 7-4 represents the ratio or normalization of the sums of the hydrocarbon types to acetylene. By comparison of these ratios to those measured in the tunnel and roadway samples, additional sources of hydrocarbons other than vehicular emission, as well as the photochemical loss of the reactive hydrocarbons, can be observed.

Table 7-4. AIRCRAFT SAMPLES TAKEN AUGUST 14, 1975 - BOSTON OXIDANT STUDY

Sample No.	Ozone, ppb	C_2H_2, ppbC	$\Sigma P/C_2H_2$	$\Sigma A/C_2H_2$	$\Sigma O/C_2H_2$	Dimethyl acetamide, ppbC
1	87	2.2	10.5	10.6	2.4	77.9
2	108	2.1	19.4	23.0	2.5	52.3
3	160	5.0	13.7	7.0	2.3	51.0
4	186	7.1	12.0	7.5	1.4	363.6
5	104	2.1	17.8	15.4	2.2	152.2
6	119	3.8	11.5	7.8	1.7	105.9
7	53	1.0	17.3	20.0	4.0	77.3
Roadway			8.9	6.0	3.6	
Ground level						18-25

In each of the aircraft samples, the $\Sigma P/C_2H_2$ were higher than those observed in the roadway samples. These higher ratios are generally observed in urban and suburban atmospheres and are usually attributed to gasoline spillage and evaporative sources. Ethane and propane were included in these calculations, and in some of these samples the high $\Sigma P/C_2H_2$ ratios observed were due to those two paraffins. A more accurate calculation would be to exclude these two compounds from consideration.

The $\Sigma A/C_2H_2$ observed in these aircraft samples were higher than those observed along the roadway. Industrial and gasoline sources may be partly responsible for these higher ratios; however, unknown peaks, possibly from the surfaces of the Tedlar bag, interfere with an accurate summation. Additional surface outgassing is indicated by the extremely high concentration of dimethylacetamide, the solvent used in the extrusion process of Tedlar. These concentrations were two to twenty times higher than those observed in ground level bag samples and are probably the result of the higher ambient temperature in the aircraft. The $\Sigma O/C_2H_2$ ratios, with the exception of bag 7, were lower than the roadway ratio, indicating photochemical loss.

In an effort to evaluate corresponding hydrocarbon data with observed ozone levels during the Northeast Oxidant Transport Study, correlations of hydrocarbons with ozone were performed. Some obvious comparisons were investigated, including the comparison of the ratios of reactive hydrocarbons to acetylene with ozone in an effort to determine whether observed ozone levels correlated with reactive hydrocarbon loss. These relationships were not that obvious since prior knowledge of the air mass, such as initial absolute concentration levels and HC/NO_x ratios, is necessary.

In an effort to investigate urban tracer relationships to ozone, acetylene and corresponding ozone data were assembled for aircraft samples. The acetylene and ozone for each individual flight appeared to have a linear relationship, especially for flights over the Atlantic Ocean during afternoon and later afternoon time periods. For this reason, correlations of acetylene versus ozone were performed by setting acetylene as the independent variable and ozone as the dependent variable. Linear regression equations were also determined. The results of these exercises are recorded in Table 7-5.

Table 7-5. CORRELATION OF OZONE VERSUS ACETYLENE FOR EPA-LV AIRCRAFT SAMPLES - BOSTON OXIDANT STUDY, 1975

Sample period	Observations	P	Slope	Intercept	O_3 range, ppb	C_2H_2 range, ppbC
August 14	7	0.91	19.6	46.1	53-186	1.0 - 7.1
August 20	7	0.95	15.9	38.1	40- 69	0.3 - 1.5
August 27	6	0.87	29.9	20.7	58-	1.6 - 2.6
All samples	66	0.85	19.4	31.0	29-186	0.2 - 7.1

Slopes and intercepts in the regression equations are reasonably comparable, as might be expected since emissions and meteorological parameters are expected to be consistent during this short study period. Differences in slopes may be due to the variation of absolute hydrocarbon and nitrogen oxides concentrations, HC/NO_x ratio, temperature, sunlight intensity or, in general, the chemical and physical parameters that control the photochemical reaction mechanism.

The intercept could represent background ozone or a condition where auto exhaust contribution is zero, since acetylene is equal to zero. The ozone in these instances would be the result of hydrocarbon and nitrogen oxides emissions from other anthropogenic sources such as power plants, gasoline evaporative and spillage emissions, and other industrial sources, along with natural background emissions for this particular area.

During the 1974 Midwest Oxidant Transport Study, an urban plume of high ozone was transported into Wilmington, OH, from the general direction of Dayton on July 18. On this particular day, the afternoon ozone increased to 0.20 ppm, a factor of two increase in the ozone concentration. The acetylene levels were also the highest observed during the entire study. The step increase in ozone was associated with a similar increase in acetylene. For this reason these two components were correlated and a linear regression curve established. The result were a slope of 15.4 and an intercept of 38 with a correlation coefficient of 0.90 for six data pairs. These values are comparable to those obtained for Boston.

Acetylene and ozone seem to be likely candidates for this type of mathematical treatment since acetylene is representative of automotive emissions - the most abundant source of photochemical smog precursors.

It must be understood that extrapolation of these linear regression equations to points other than actual data pairs are purely speculative. This exercise, however, is extremely interesting since background levels of ozone predicted by these calculations are comparable to actual experimental observations such as the 30 ppb ozone measurements made over Maine during the flight of August 28, 1975. The corresponding acetylene levels for these hydrocarbon samples ranged from 0.2 to 0.5 ppb acetylene.

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8. TRENDS IN OZONE LEVELS IN SOUTHERN NEW ENGLAND FOR 1975

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This presentation will summarize observed photochemical oxidant concentrations in Connecticut, Massachusetts, and Rhode Island for April through September 1975 and discuss some interesting trends observed during the months of July and August (the Northeast Oxidant Transport Study was conducted July 15 through August 28, 1975). Data were collected at state-operated monitoring stations using continuous chemiluminescent ozone monitoring instruments. These data are recorded in the SAROAD system. Eastern standard time was used in all cases.

The locations of ozone monitoring stations are shown on the map of southern New England (Connecticut, Massachusetts, and Rhode Island) in Figure 8-1. In 1975, 14 monitoring stations were operated by Connecticut (Derby was not operational), 21 by Massachusetts, and 2 by Rhode Island. The letters (A-D) show the locations of the special monitoring stations for the summer oxidant study as follows: A--Environmental Protection Agency, Research Triangle Park, at Quincy; B--Washington State University at Groton; C--Battelle at Simsbury; and D--Harvard School of Public Health at Watertown. Table 8-1 describes the locations and instrumentation for the state ozone monitoring stations.

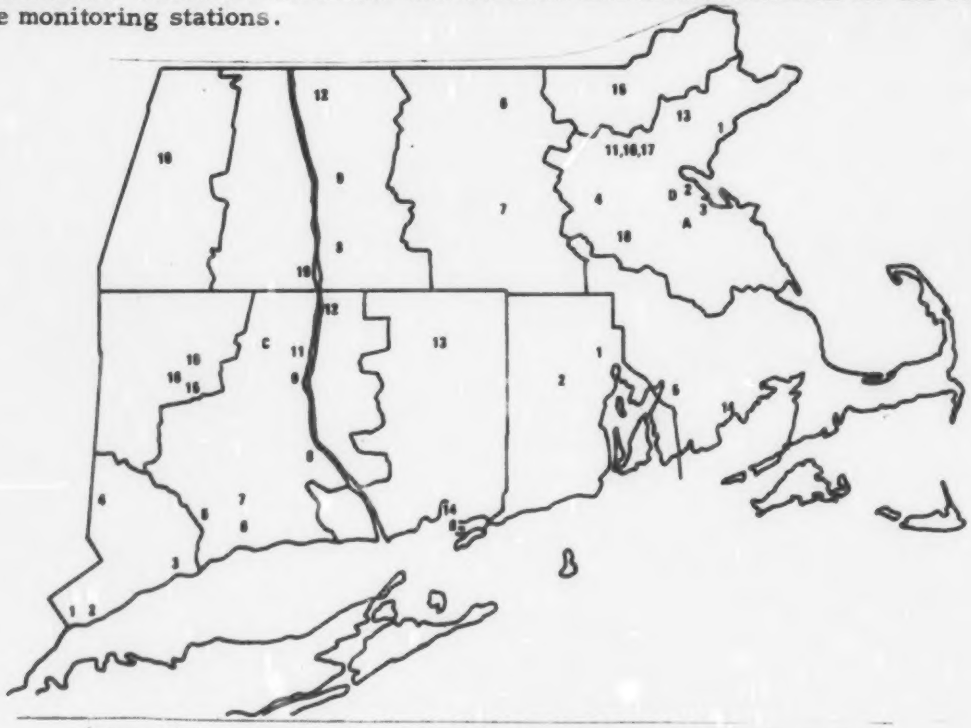

Figure 8-1. Location of ozone monitoring stations operating in southern New England during 1975 Oxidant Transport Study.

Table 8-1. MONITORING SITES

City	Location	Local environs
	Connecticut sampling sites	
1. Greenwich	Bruce Golf Course	Rural
2. Stanford	Trailer at Health Department	Urban
3. Bridgeport	Barnum Avenue, Housatonic Community College	Urban
4. Danbury	W. Connecticut State College	Suburban
5. Derby	Flood control dam (not operational 1975)	Urban
6. New Haven	Agricultural experimental station	Suburban
7. Hamden	Agricultural experimental station	Rural
8. Middletown	City Hall	Urban
9. Hartford	State office building	Urban
10. Torrington	Franklin Avenue	Urban
11. Windsor	Agricultural experimental station	Rural
12. Enfield	Kosciusko School	Suburban/rural
13. Eastford	Natchaug State Forest	Rural
14. Groton	Fort Griswold	Suburban
15. Litchfield	Morris, Route 109	Rural
	Massachusetts sampling sites	
1. Salem	New high school, Highland Ave.	Suburban
2. Cambridge	Science Park Monsignor O'Brien Highway	Urban
3. Quincy	Fore River Bridge traffic circle	Suburban
4. Framingham	Civil Defense - Route 9	Suburban/rural
5. Fall River	Globe Street Fire Station	Suburban
6. Fitchburg	Summer Street Substation	Suburban/rural
7. Worcester	New Salem & Washington Streets	Urban
8. Chicopee	Westover Air Force Base (operational 7-15-75)	Suburban
9. Amherst	University of Massachusetts	Suburban
10. Pittsfield	Dalton Ave. (state police barracks)	Suburban/urban
11. Medford	Wellington Circle, Rts. 28 & 16	Suburban
12. Greenfield	Waste water treatment facility	Rural
13. Danvers	Essex Agricultural College	Rural/suburban
14. Fairhaven	Marina - Middle Street	Suburban
15. Lowell	John Street trailer	Urban
16. Waltham	Moody & Main Street	Urban
17. Waltham	Beaver Street	Suburban
18. Medfield	State Hospital	Rural
19. Springfield	E. Columbus Ave.	Urban
20. Boston	Kenmore Square	Urban
21. Boston	J.F.K. Building (25th floor)	Urban
	Rhode Island sampling sites	
1. Providence	State Street	Urban
2. Scituate	Scituate Reservoir	Rural

Monthly maximum ozone values and frequency of violations for April through September 1975 in Connecticut, Massachusetts, and Rhode Island are presented in Tables 8-2 to 8-4, respectively. Four general observations can be made regarding these data:

1. Violations of the National Ambient Air Quality Standard for photochemical oxidants occurred throughout the 6-month period from April to September 1975 in Southern New England.

2. Maximum ozone levels for this period were recorded in June for all three states.

3. Violations of the photochemical oxidant standard tended to occur most frequently at rural and suburban/rural locations.

4. Furthermore, in Connecticut and Massachusetts the photochemical oxidant standard tended to be violated most frequently at particular locations:

    a. In Massachusetts, for April through July the site with the most frequent violations was Framingham, which is located approximately 19 miles west of Boston.

    b. In Connecticut, for May, June, and July the most frequent violations occurred at Torrington or Litchfield, which are in the same general area in northwestern Connecticut.

Table 8-2. MONTHLY MAXIMUM OZONE VALUES AND FREQUENCY OF VIOLATIONS, APRIL THROUGH SEPTEMBER, 1975, CONNECTICUT

	April	May	June	July	August	September
Site with lowest maximum[a]	New Haven 0.050/0	Greenwich 0.159/11	Stamford 0.125/6	Windsor 0.130/11	Windsor 0.095/4	Windsor 0.070/0
Site with highest maximum[a]	Windsor 0.090/1	Bridgeport 0.245/9	Middletown 0.325/6	New Haven 0.315/13	New Haven 0.190/6	Eastford 0.125/5
Site with most frequent violations[b]	Eastford 3/2	Torrington 38/16	Torrington 54/9	Litchfield 179/19	Groton 119/16	Hamden 5/2
Number of sites with violations[c]	4/12	11/11	11/11	14/14	14/14	7/14

[a] Maximum value in parts per million/number of days standard (0.08 ppm for 1 hour) exceeded.

[b] Number of violations/number of days.

[c] Number of sites with violations/number of sites operational.

Figures 8-2 to 8-5 present monthly maximum and monthly average ozone concentrations by hour of the day (Eastern Standard Time) for July and August at selected locations. Bridgeport (Figures 8-2a and 8-2b) was selected as generally representative of Connecticut data, particularly the urbanized areas. For both July and August, high oxidant levels were measured in the afternoon. However, a different pattern

TABLE 8-3. MONTHLY MAXIMUM OZONE VALUES AND FREQUENCY OF VIOLATIONS, APRIL THROUGH SEPTEMBER 1975, MASSACHUSETTS

	April	May	June	July	August	September
Site with lowest maximum[a]	Springfield 0.046/0	Boston 0.080/0	Springfield 0.060/0	Springfield 0.080/0	Boston 0.090/3,056/0	Cambridge
Site with highest maximum[a]	Cambridge 0.100/1	Amherst 0.200/10	Framingham 0.208/6	Pittsfield 0.168/7	Fairhaven 0.75/14	Waltham, Beaver St. 0.150/5
Site with most frequent violations[b]	Framingham 3/1	Framingham 66/12	Framingham 32/6	Framingham 79/4	Fairhaven /14	Waltham 23/5
Number of sites with violations[c]	3/14	13/14	12/15	17/18	17/17	13/17

[a] Maximum value in parts per million/number of days standard (0.08 ppm for 1 hour) exceeded.

[b] Number of violations/number of days.

[c] Number of sites with violations/number of sites operational.

Table 8-4. MONTHLY MAXIMUM OZONE VALUES AND FREQUENCY OF VIOLATIONS, APRIL THROUGH SEPTEMBER 1975, RHODE ISLAND

	April	May	June	July	August	September
Site with lowest maximum[a]	No data	Providence 0.125/4	Scituate 0.150/3	Scituate 0.110/6	Scituate 0.095/3	Scituate 0.045/0
Site with highest maximum[a]	No data	Scituate 0.135/7	Providence 0.180/3	Providence 0.135/8	Providence 0.105/7	Providence 0.110/1
Site with most frequent violations[b]	No data	Scituate 50/7	Scituate 22/3	Providence 36/8	Providence 17/7	Providence 6/1
Number of sites with violations[c]	No data	2/2	2/2	2/2	2/2	1/2

[a] Maximum value in parts per million/number of days standard (0.08 ppm for 1 hour) exceeded.

[b] Number of violations/number of days.

[c] Number of sites with violations/number of sites operational.

was observed for Eastford, CN, which is a rural site in the northeastern portion of the state. In July (Figure 8-3a), the highest oxidant levels occurred in the late afternoon and evening hours. The monthly average ozone curve is also skewed toward the late afternoon. The pattern for August (Figure 8-3b) is not quite as pronounced, but violations also occurred in the late afternoon and nighttime hours.

The departure from the standard diurnal curve for maximum ozone values tended to be even more pronounced in Massachusetts. In Framingham (Figure 8-4a), the highest ozone levels during July occurred in the evening, although violations also occurred in the morning and afternoon. As in Eastford, the Framingham pattern during August (Figure 8-4b) is not pronounced, although the highest ozone levels occurred in the late afternoon.

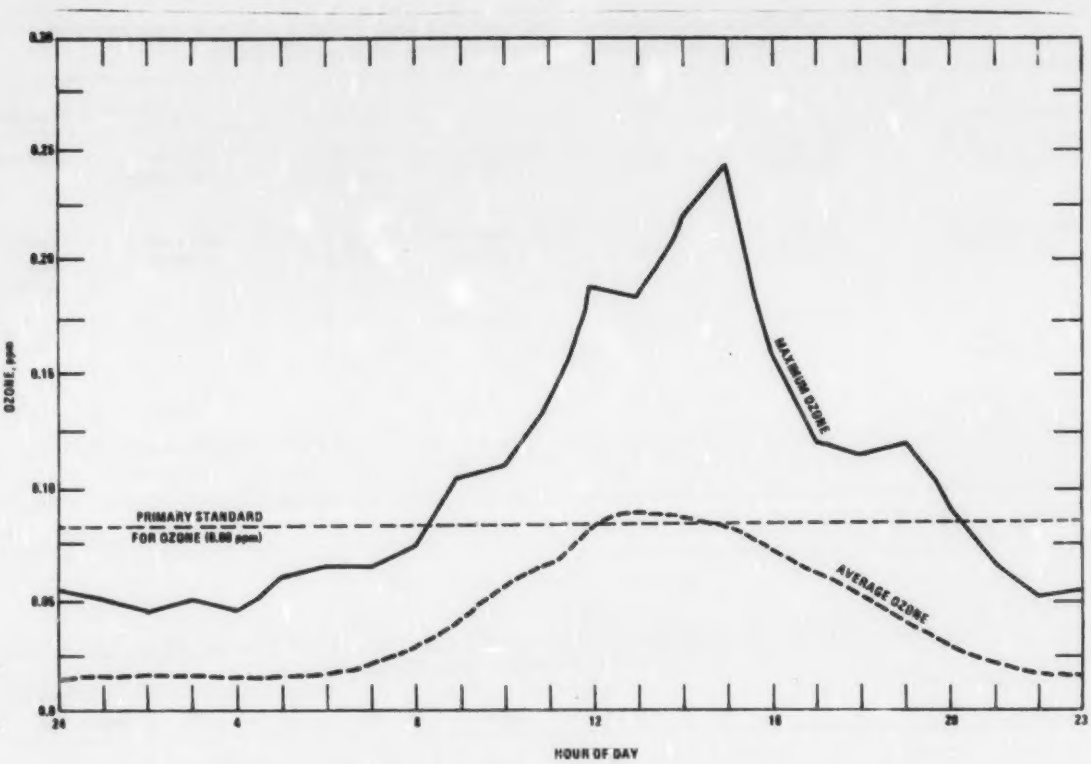

Figure 8-2a. Monthly maximum and average ozone concentrations by hour for Bridgeport, Conn., July 1975.

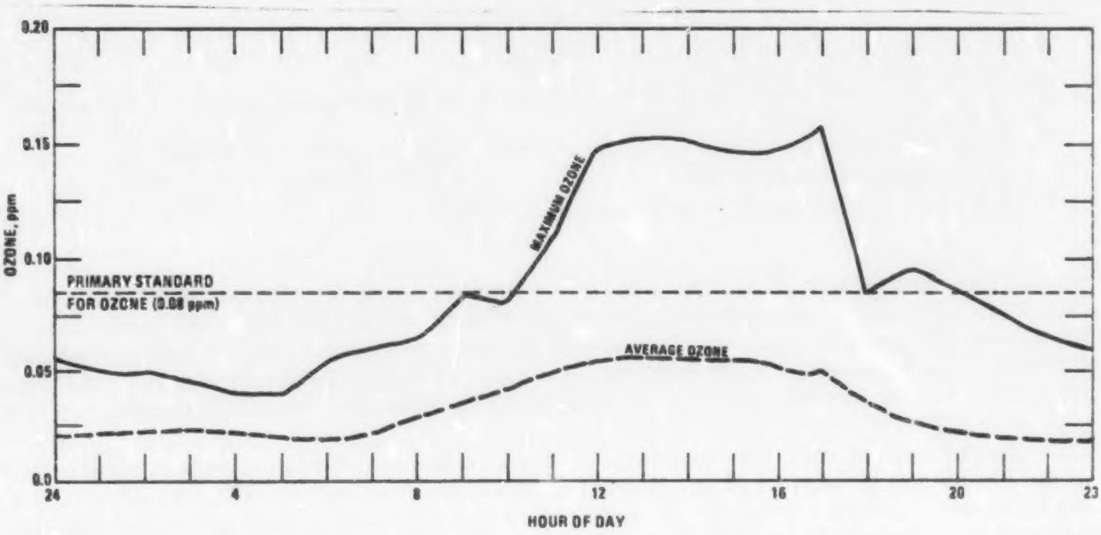

Figure 8-2b. Monthly maximum and average ozone concentrations by hour for Bridgeport, Conn., August 1975.

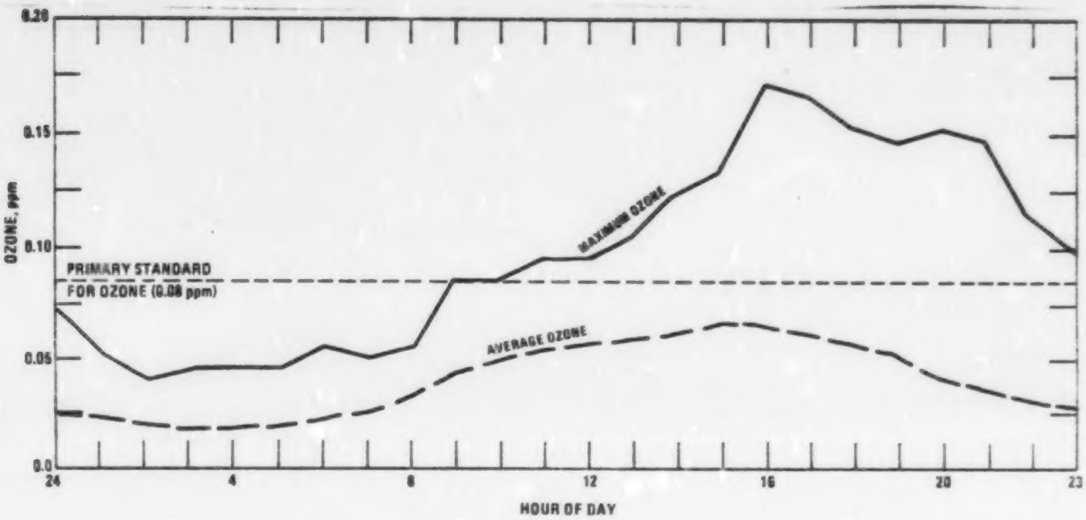

Figure 8-3a. Monthly maximum and average ozone concentrations by hour for Eastford, Conn., July 1975.

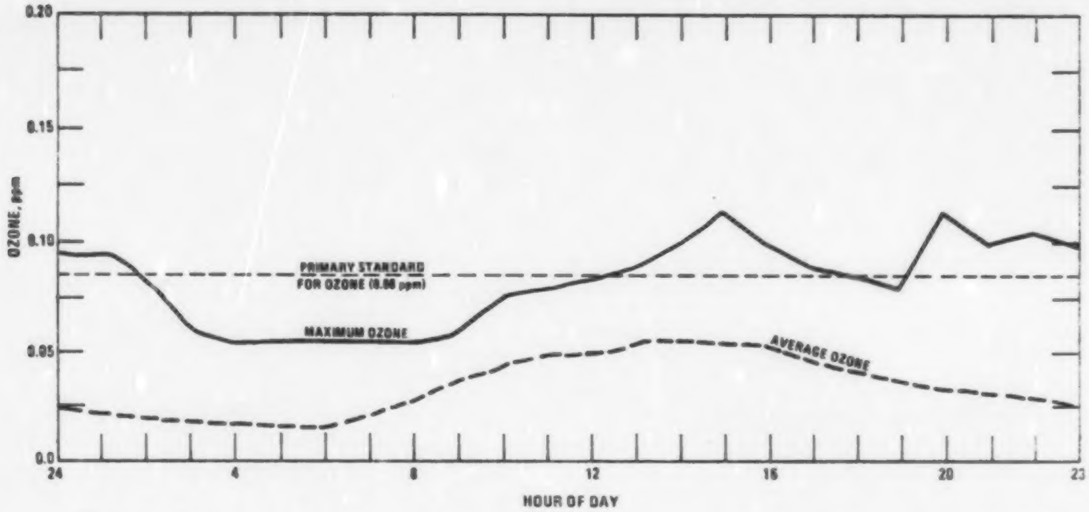

Figure 8-3b. Monthly maximum and average ozone concentrations by hour for Eastford, Conn., August 1975.

By comparing the July data for Bridgeport, Eastford, and Framingham, it is apparent that the highest ozone values occurred later in the day (from midafternoon to late evening) as one moves to the northeast. However, the monthly average ozone concentrations by hour of the day shift very little. It is expected that this is due to a greater frequency of daily maximums occurring in the afternoon while the highest monthly maximums occurred during episode conditions, with winds probably from the southwest.

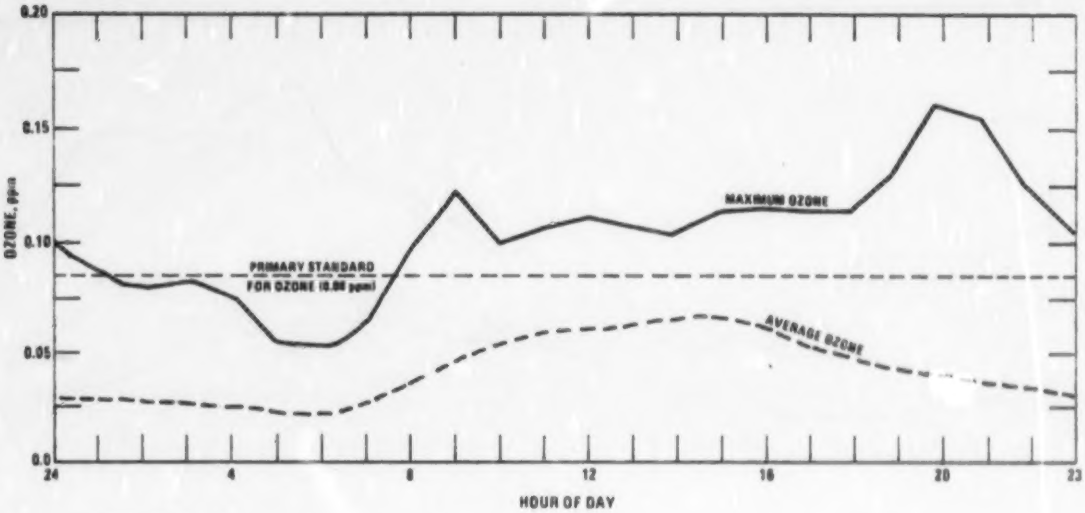

Figure 8-4a. Monthly maximum and average ozone concentrations by hour for Framingham, Mass., July 1975.

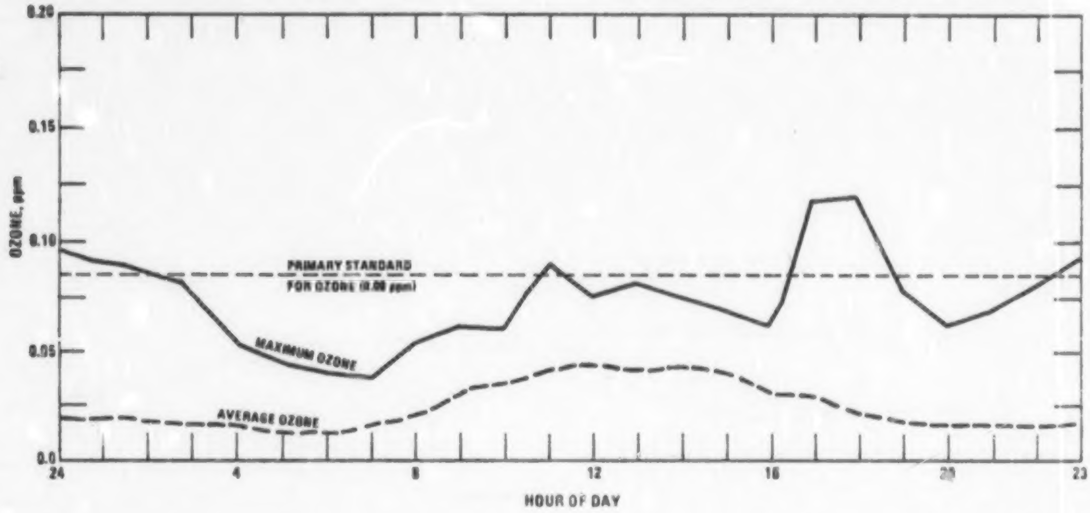

Figure 8-4b. Monthly maximum and average ozone concentrations by hour for Framingham, Mass., August 1975.

Very different patterns were observed in Litchfield, CN, a rural site approximately 25 miles west-southwest of Hartford (Figures 8-5a and 8-5b). In July, violations of the oxidant standard were observed at all hours of the day. However, there was a slight tendency for the highest ozone values to occur in the morning. A similarly uniform pattern occurred in August, although the highest ozone values were recorded in the late afternoon. Even more interesting are the monthly average ozone concentrations by hour. For both July and August, the highest monthly average ozone value occurred in the morning.

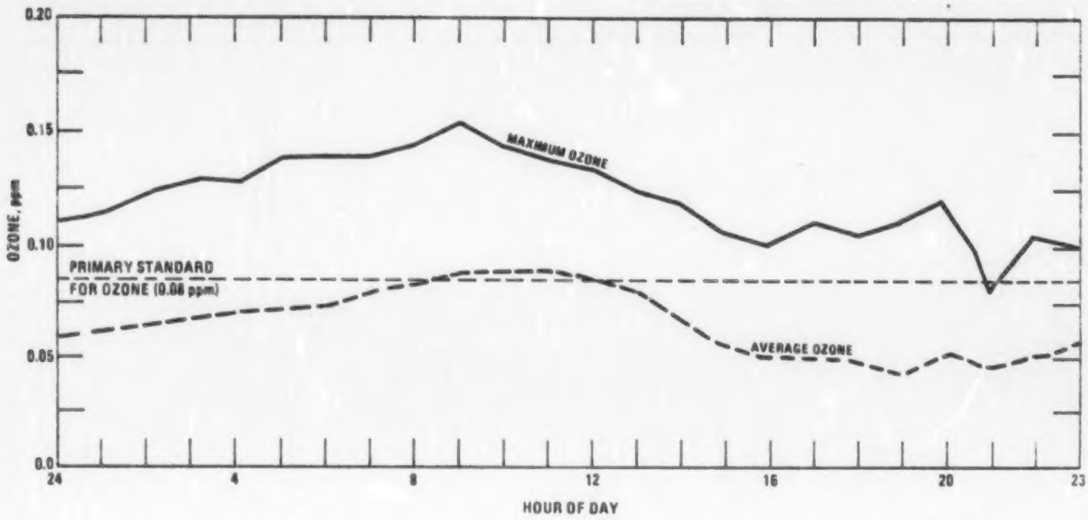

Figure 8-5a. Monthly maximum and average ozone concentrations by hour for Litchfield, Conn., July 1975.

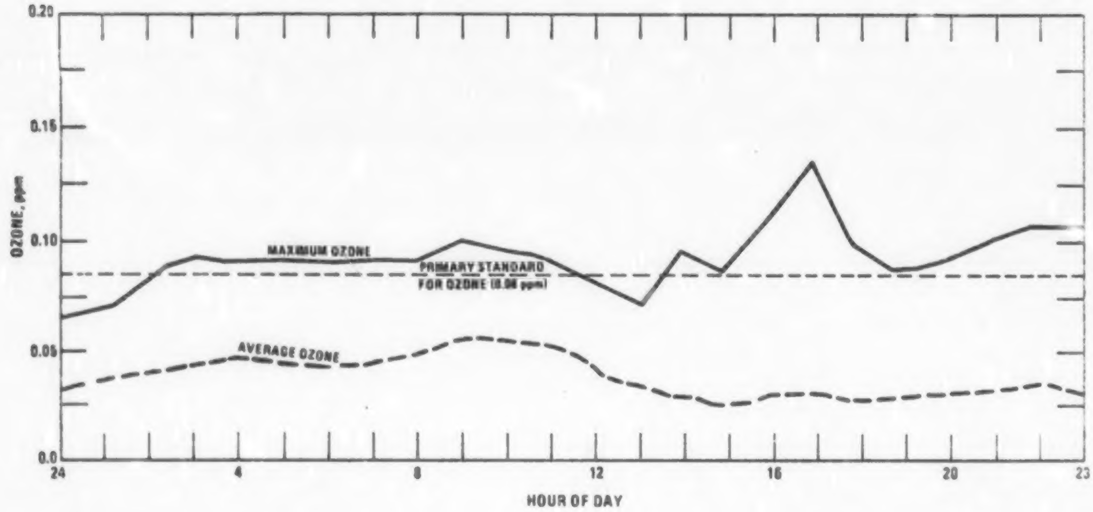

Figure 8-5b. Monthly maximum and average ozone concentrations by hour for Litchfield, Conn., August 1975.

Daily maximum ozone levels for various locations in Connecticut, Massachusetts, and Rhode Island during July and August are shown in Figures 8-6 through 8-12. Figures 8-6a and 8-6b present the daily maximum ozone levels in Middletown, CN, for July and August, respectively. Middletown was selected because the daily pattern of ozone levels is quite representative of Connecticut monitoring sites. From these graphs, one can readily see the days in which ozone violations were recorded and also pick out the "episodes." Once again, the exception to the general rule in Connecticut is the Litchfield site. The daily maximum and daily average ozone levels for Litchfield in July are presented in Figure 8-7 (not enough data were available

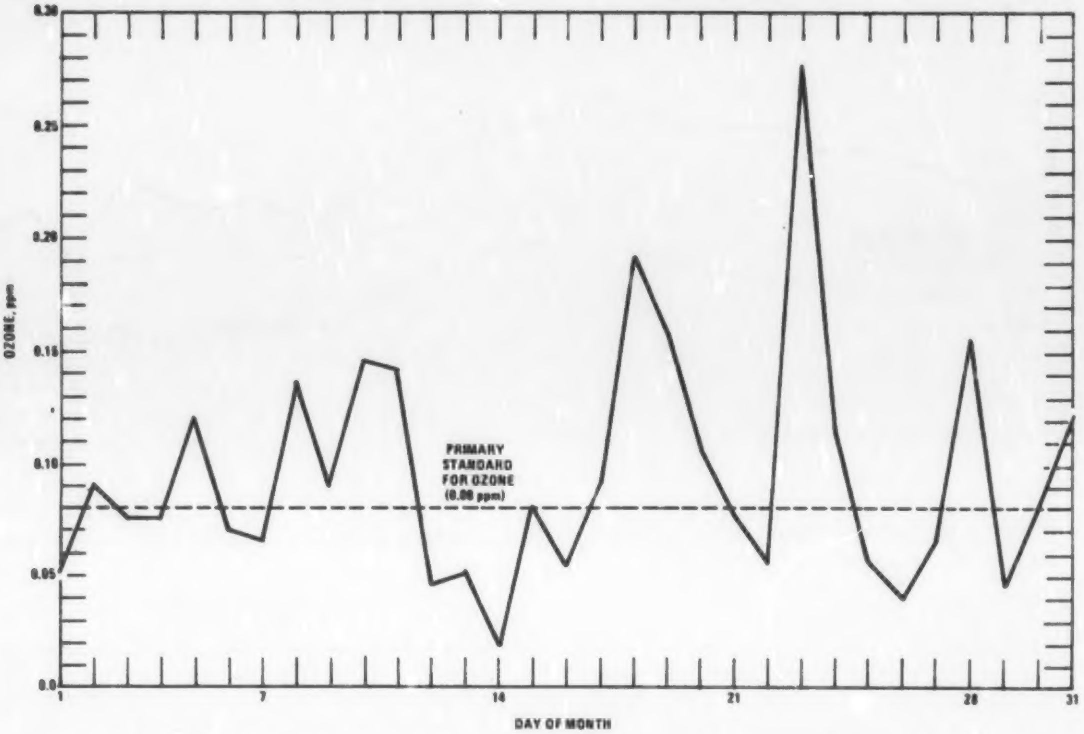

Figure 8-6a. Daily maximum ozone concentration at Middletown, Conn., July 1975.

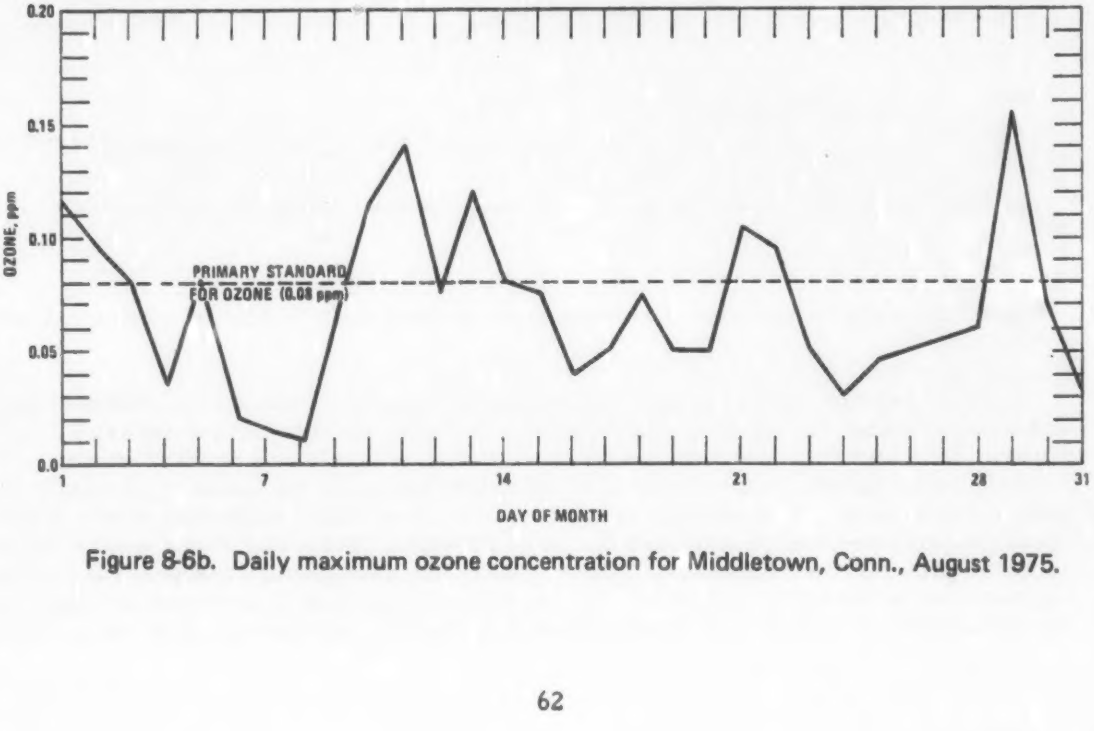

Figure 8-6b. Daily maximum ozone concentration for Middletown, Conn., August 1975.

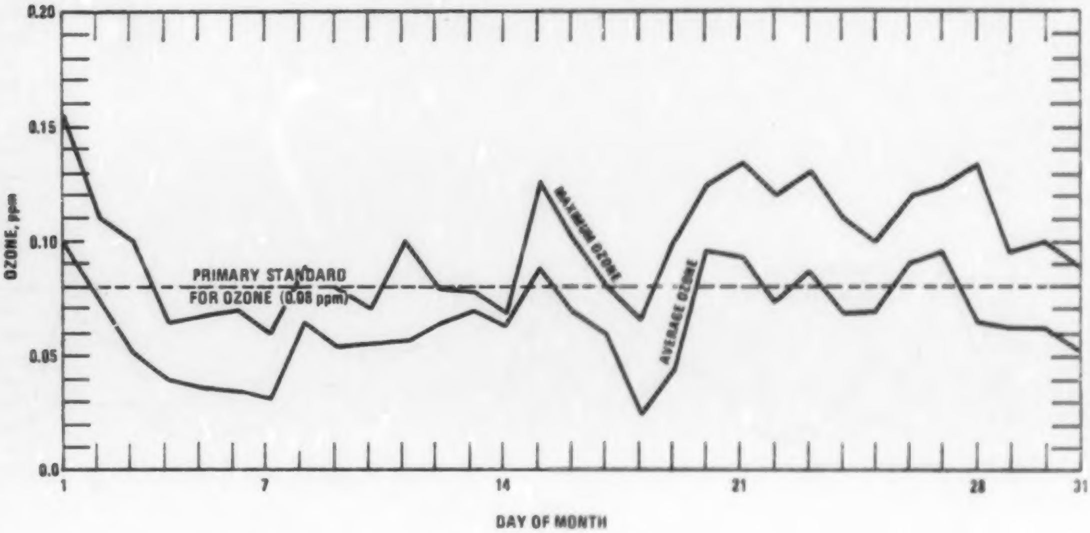

Figure 8-7. Daily maximum and average ozone concentrations for Litchfield, Conn., July 1975.

to present a graph of August daily levels). By comparing the Litchfield data (Figure 8-7) to the Middletown data (Figure 8-6a), one can readily see that the Litchfield site does not show the variation in daily maximum oxidant levels found at Middletown. Furthermore, days on which peak ozone levels were measured at Litchfield frequently do not correspond to days on which peak ozone levels were measured at Middletown. Daily average ozone levels for Litchfield are also shown in Figure 8-7 to illustrate the fact that ozone levels tended to remain elevated during the nighttime hours, resulting in daily average values being in violation of the standard on several occasions.

Figures 8-8a and 8-8b present daily maximum and daily average ozone concentrations for Scituate, RI, during July and August. Although the values are much lower than those measured in Middletown, CN, the same general patterns in the day-to-day fluctuations of ozone levels were observed. These same patterns of day-to-day fluctuations in ozone levels for July and August were also observed at Framingham, MA (Figures 8-9a and 8-9b).

Although the daily maximum oxidant levels recorded at Framingham in July were representative of Massachusetts in general, in August a very different situation emerged; oxidant levels in Massachusetts varied along a north-south axis, with the highest levels being found in southeastern Massachusetts. In Danvers, which is located northeast of Boston, daily maximum ozone levels in July (Figure 8-10a) are comparable to those in Framingham (Figure 8-9a), but in August, ozone levels at Danvers (Figure 8-10b) were generally lower than those measured in Framingham. On the other hand, daily maximum ozone levels measured in August at Fairhaven, MA (Figure 8-11), which is located in southeastern Massachusetts on the coast of Buzzard's Bay, were generally much higher than those measured in Framingham (Figure 8-9b). (Insufficient data were available to graph the daily maximum ozone levels for July at Fairhaven.) In addition, the daily maximum ozone values measured in August at Fairhaven were very similar to those measured at Groton, CN (Figure 8-12), which is located approximately 60 miles west-southwest of Fairhaven. Fairhaven and Groton were also the sites with the most frequent violations in their respective states

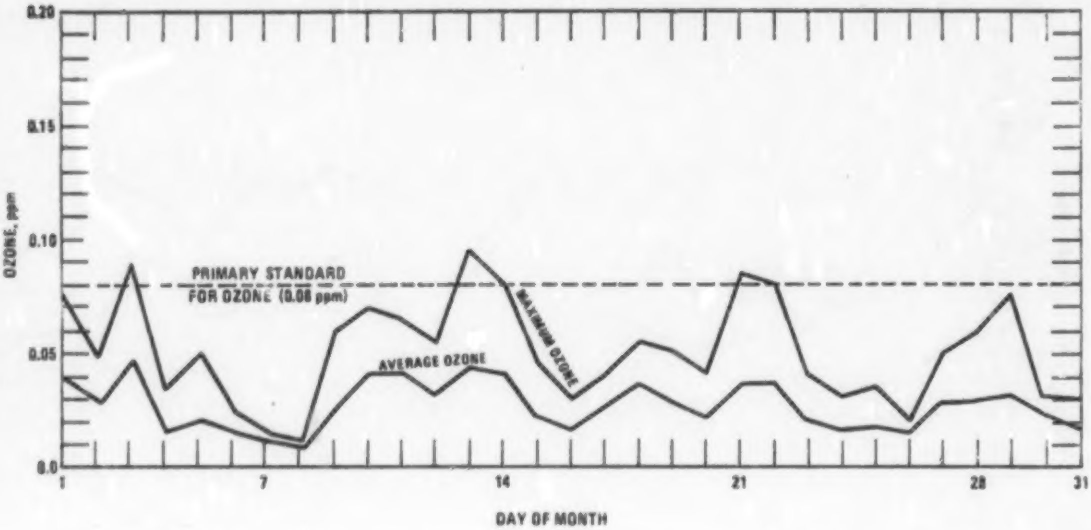

Figure 8-8a. Daily maximum and average ozone concentrations for Scituate, R.I., July 1975.

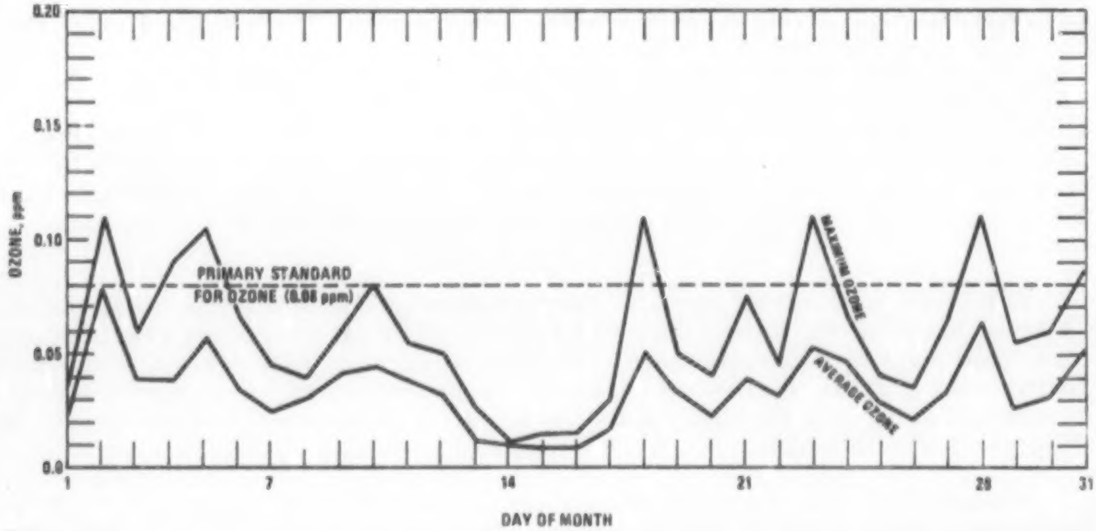

Figure 8-8b. Daily maximum and average ozone concentrations for Scituate, R.I., August 1975.

in August (Tables 8-2 and 8-3), and the highest ozone level for August in Massachusetts was recorded at Fairhaven (Table 8-3).

These observations are believed to be significant with respect to the different meteorological conditions experienced in New England in July and August. Specifically, from preliminary review of meteorological data, it appears that northwest wind flow was experienced more frequently in August and south to southwest wind flow more frequently in July. The similarity of the Fairhaven and Groton data in August would certainly be consistent with northwesterly wind trajectories. This effect of meteorological conditions on ozone levels will be more thoroughly studied.

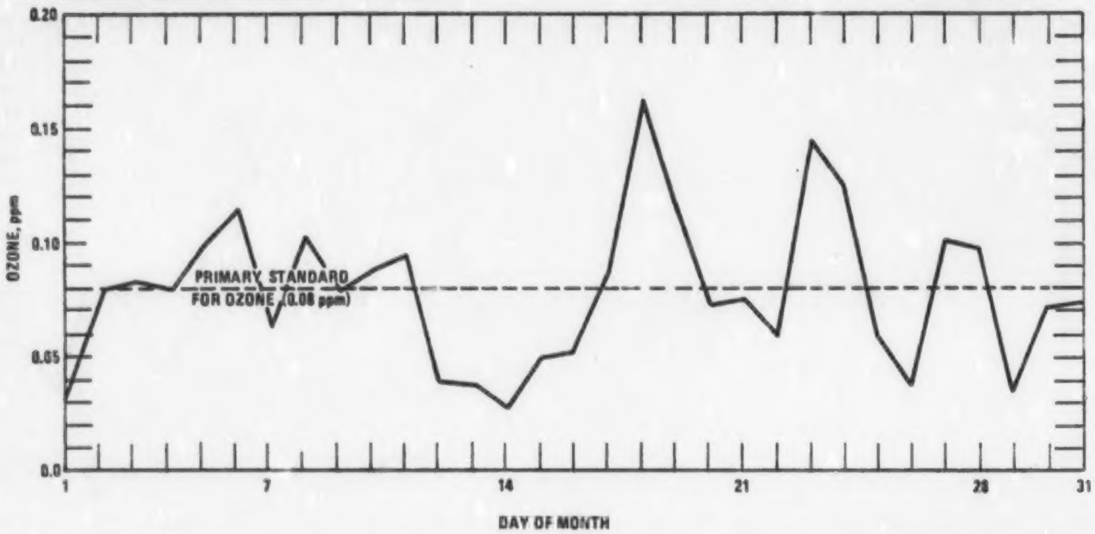

Figure 8-9a. Daily maximum ozone concentration for Framingham, Mass., July 1975.

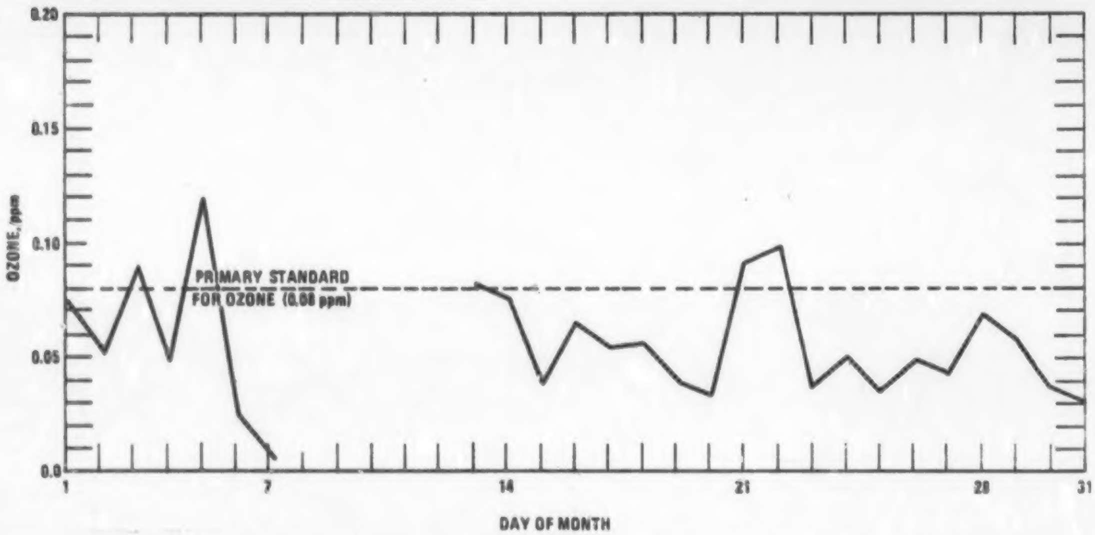

Figure 8-9b. Daily maximum ozone concentration for Framingham, Mass., August 1975.

Finally, hourly ozone data are presented for the air pollution episode of July 23-24, 1975. This period was selected because it was the major episode during the summer study (i.e., the highest measured ozone levels). In addition, the surface wind flow was from the southwest, a situation in which one would expect to find maximum transport of pollutants into southern New England.

Hourly ozone levels for various locations in Connecticut are presented in Figure 8-13. As can be seen, the daily maximum ozone concentrations occurred later in the

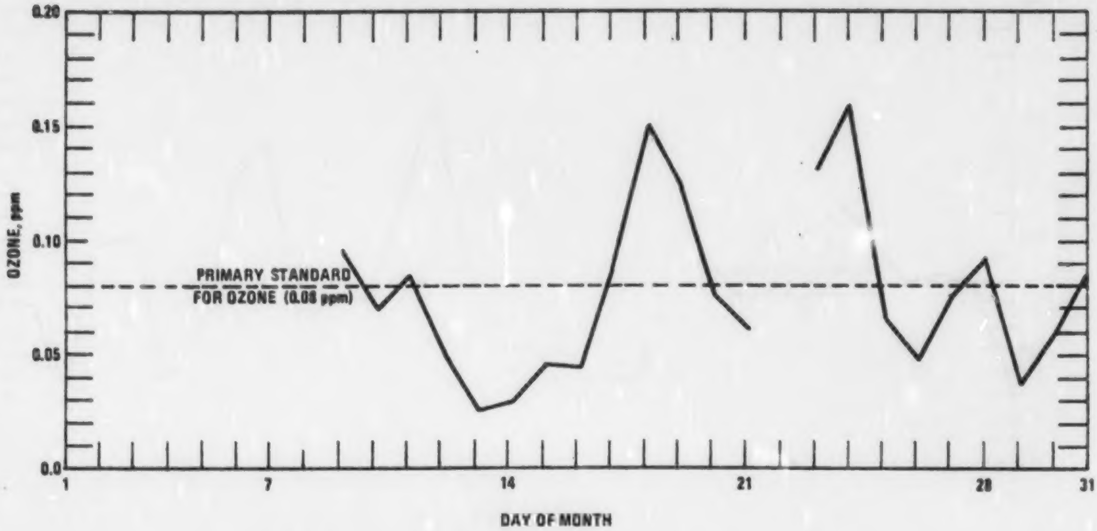

Figure 8-10a. Daily maximum ozone concentration for Danvers, Mass., July 1975.

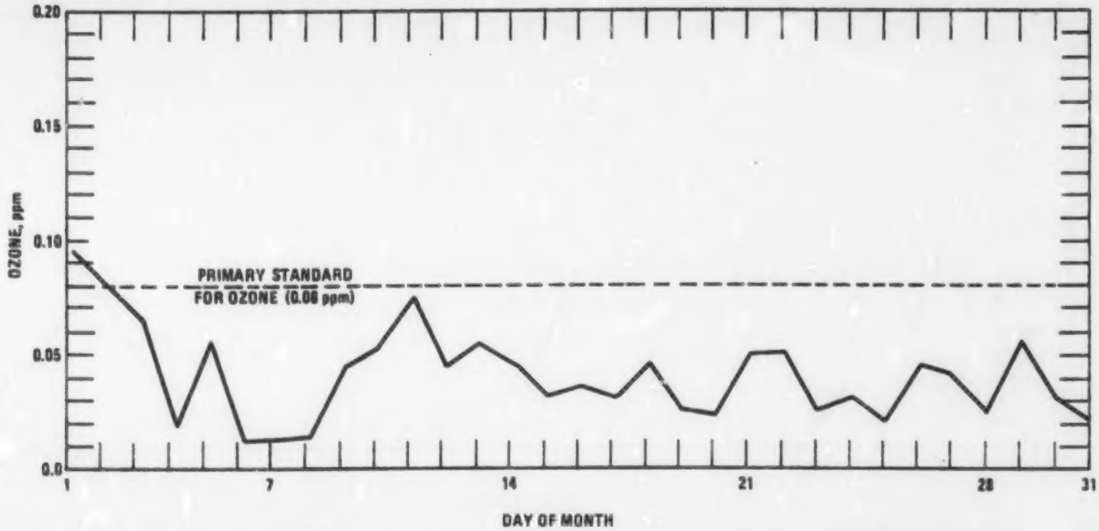

Figure 8-10b. Daily ozone concentration for Danvers, Mass., August 1975.

afternoon at monitoring sites along a northeasterly trajectory. Specifically, the daily maximums on July 23rd, occurred at 1200 in Greenwich, at 1500 in New Haven, and 1600 in Eastford.

This trend of later daily maximum ozone levels occurring along a northeasterly trajectory continued in Rhode Island and Massachusetts. As presented in Figure 8-14, on July 23 the daily maximum ozone levels in Rhode Island occurred at 1700 in Scituate and 1800 in Providence. In Massachusetts (Figure 8-15), the daily maximum ozone levels on July 23 occurred in the evening: Framingham at 1800, Danvers at

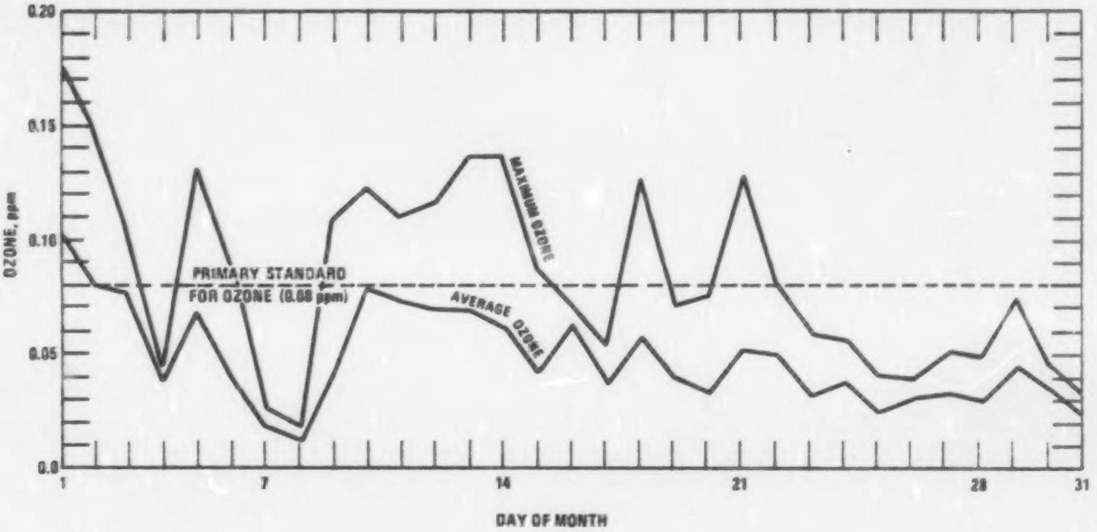

Figure 8-11. Daily maximum and average ozone concentrations for Fairhaven, Mass., August 1975.

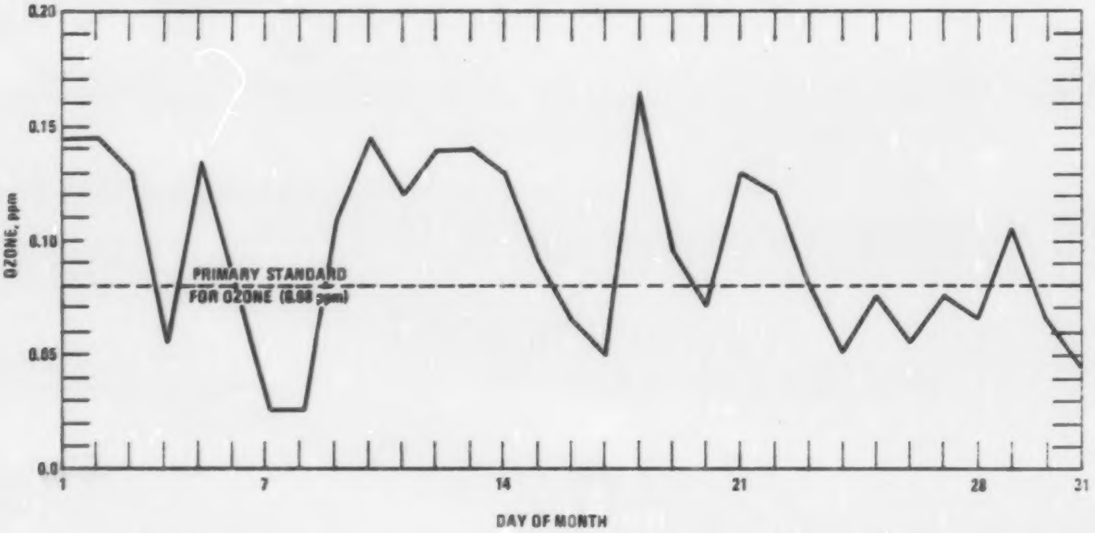

Figure 8-12. Daily maximum ozone concentration for Groton, Conn., August 1975.

2000, and Fairhaven (east of Rhode Island) at 2100. Furthermore, it is interesting to note that the July 24 daily maximum ozone levels at Danvers and Framingham occurred at 0800 and 0900, respectively.

Although no definite conclusions can be drawn from these data, transport of oxidants and oxidant precursors is strongly indicated. Also, during this episode it appears that transport may have occurred up the Connecticut River Valley on July 24, 1975. Hourly ozone values on July 24 measured in Connecticut and Massachusetts

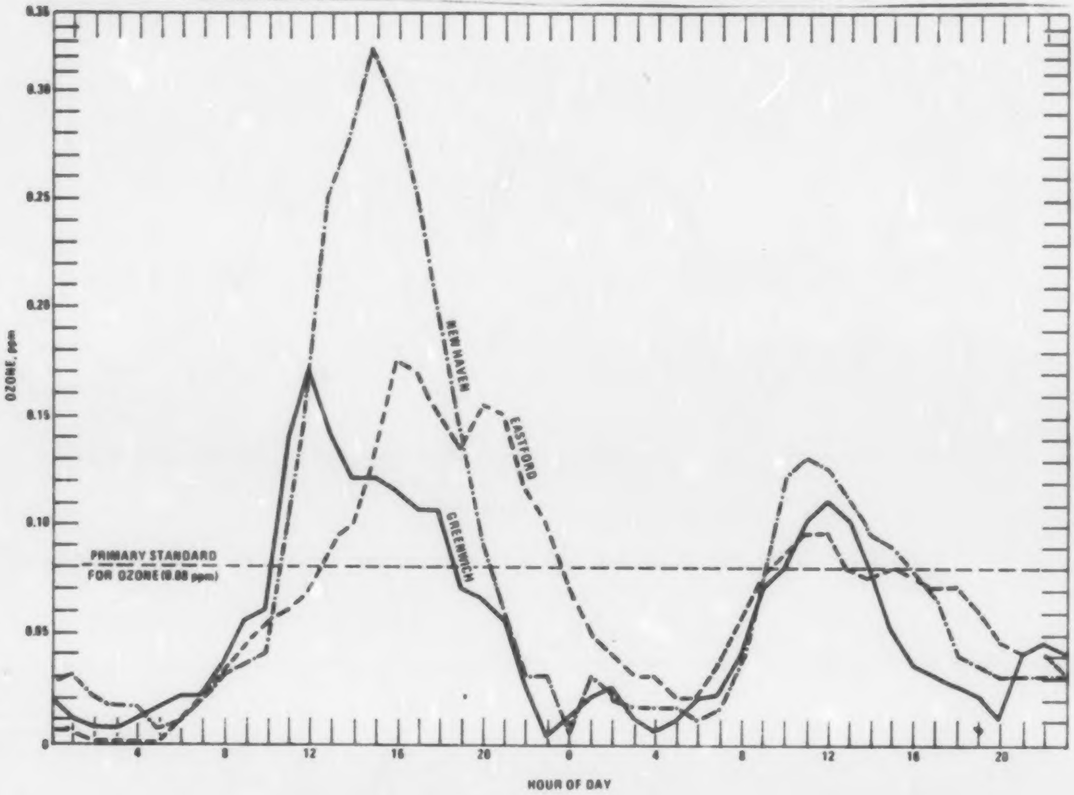

Figure 8-13. Hourly ozone concentrations at three Connecticut sites, July 23-24, 1975.

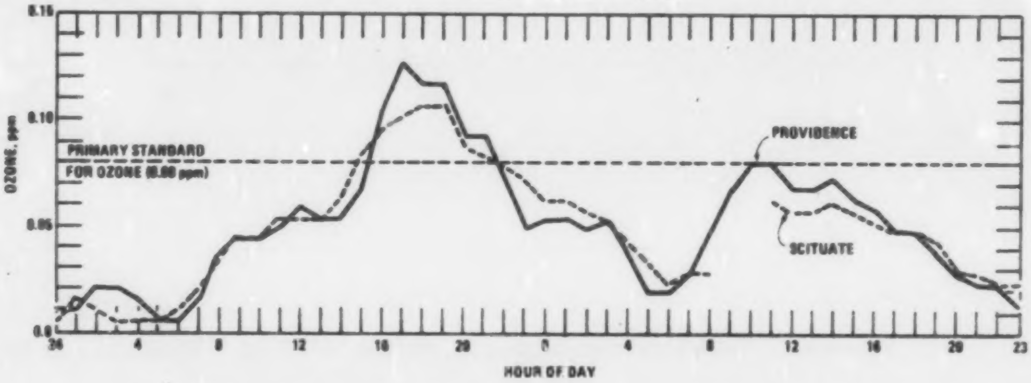

Figure 8-14. Hourly ozone concentration at the two Rhode Island sites, July 23-24, 1975.

within the Connecticut River Valley are presented in Figure 8-16. Daily maximum ozone values were measured later in the day at the more northerly sites up the Connecticut River Valley: Middletown at 1100, Hartford at 1200, Enfield at 1300, Amherst at 1400. Whether this may be transport of ozone generated within the valley itself or channeling of ozone from the larger air mass mixed with locally generated pollution remains to be determined. This is another issue that will be studied in the evaluation of the summer data that will be conducted during the next several months.

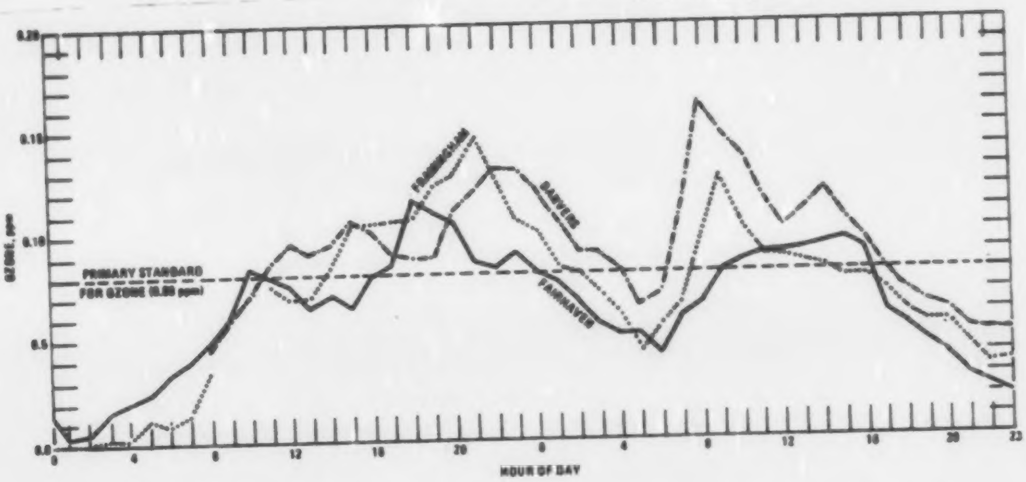

Figure 8-15. Hourly ozone concentration at three Massachusetts sites, July 23-24, 1975.

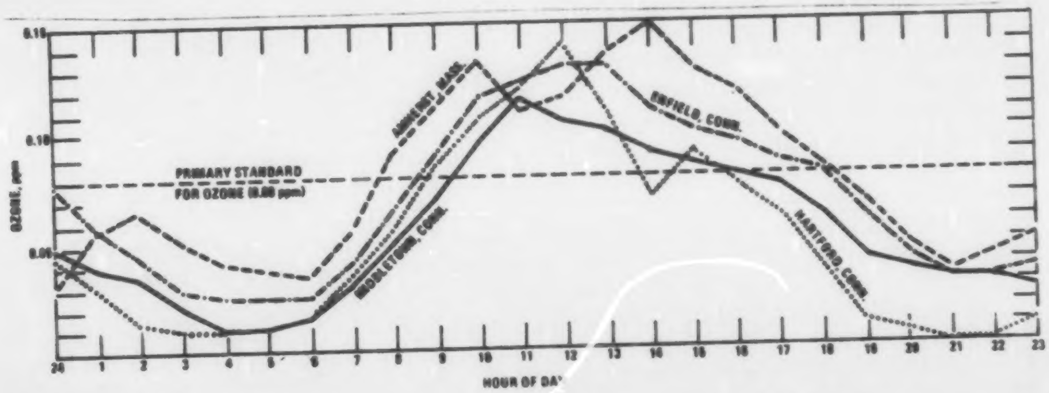

Figure 8-16. Hourly ozone concentrations at four New England sampling sites.

9. AERIAL INVESTIGATION OF PHOTOCHEMICAL OXIDANTS OVER THE NORTHEAST

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Ralph E. Pasceri
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INTRODUCTION

For the past 3 years the Interstate Sanitation Commission has been coordinating a study to investigate the phenomenon of elevated ozone levels in the tristate (New York, New Jersey, Connecticut) area. Other participants in the study were the states of New York, New Jersey, and Connecticut, the city of New York, and the U.S. Environmental Protection Agency (EPA), Region II, Surveillance and Analysis Group. The study has included intensive surface monitoring at urban and rural sites, vertical profile sampling, hydrocarbon analysis, and aerial surveillance. During the period of August 10-22, 1975, the Commission, on behalf of and in cooperation with the states of New Jersey, Connecticut, and New York, was funded by EPA to conduct additional aerial ozone sampling. In addition to approximately 60 hours of flight time funded by EPA, some flight time was funded by the New Jersey Department of Environmental Protection. This paper describes some of the results of these flights.

The area included in the sampling program was within the Washington, DC, to Boston, MA, corridor and extended from northeastern Maryland to southern Connecticut. This included sections of EPA Regions I, II, and III. The purpose of these flights was to provide data in support of EPA's Northeast Oxidant Transport Study, conducted in Region I. Since the most significant wind direction for the production and transport of ozone in the northeastern part of the United States is from the southwest, it was important that the Region I study include similar data recorded in the regions to the southwest (upwind) of Region I. Consequently, all of the flights and flight patterns were coordinated with the meteorologist in charge of the EPA Region I study.

PROCEDURES

All of the aerial sampling was conducted using a Cessna 172 single engine aircraft. Sampling lines were extended out over the wing from the cabin air intake port. The location of the sampling line was to assure that there was no contamination from the aircraft exhaust.

Ozone measurements were obtained using an AID portable chemiluminescent ozone unit, while a Gardner Association condensation nuclei counter was used to measure condensation nuclei. Hydrocarbon samples were obtained by pulling the sample into a syringe, which was subsequently evacuated into a Tedlar bag. This procedure was repeated until there was a sufficient sample in the bag. The bags were then analyzed at either the Interstate Sanitation Commission's laboratory in New York City or the

New Jersey Department of Environmental Protection's laboratory in Trenton, NJ. Temperature measurements were obtained from the aircraft's thermometer, and wind speed and direction were obtained either from Philadelphia or from the JFK Airport prior to takeoff.

On most days, four flights were conducted: two in the morning and two in the afternoon. Flights originated from Stratford, CN, and Trenton, NJ. The flights from Stratford were manned by personnel from Connecticut Department of Environmental Protection and the Interstate Sanitation Commission, while the flights that originated from Trenton were manned by personnel from the New Jersey Department of Environmental Protection and the Interstate Sanitation Commission. Flights were conducted on August 10,11 (northern route only), 15,19,20, and 21.

QUALITY ASSURANCE

In the spring of 1975, the Commission initiated a regional quality assurance program for ozone calibrations. The Commission's ozone generator was calibrated with the neutral buffered potasium iodide (KI) method and a Dasibi ultraviolet photometer at the National Bureau of Standards (NBS). The KI calibration was used as the reference method for this study. After the initial NBS calibration, the generator was used to check the calibration of the generators maintained by New Jersey, New York, and Connecticut, and EPA Regions I and II. All calibrations were within 7 percent of the NBS calibrated concentrations. Subsequently, the Commission's generator was returned to NBS twice during the summer for recalibration, with followup checks made on the states' generators. This ensured a continuation of the uniform calibration across the region during the summer.

RESULTS AND DISCUSSION

The first point we wish to emphasize relates to the levels of ozone contained in the air mass entering the New Jersey-New York-Connecticut area. We have previously stated that the air transported into the area frequently contains ozone levels exceeding the National Ambient Air Quality Standard.[1] On several of the days during which flights were conducted, the data indicated that the air mass entering the region exceeded 80 ppb prior to traveling over either major urban area (Philadelphia-Camden-Wilmington or New York City-northeast New Jersey) in the region.

With northwest winds prevailing on August 10 and 20 (Figures 9-1 and 9-2), the air entering the Philadelphia-Camden-Wilmington complex from the northwest contained ozone levels in excess of 80 ppb. On the morning of August 10, the average upwind concentration was 120 ppb, while on August 21 (Figure 9-3), the air entering the same area from the south-southwest contained an average of 136 ppb in the afternoon. On northwest winds, Figure 9-4 shows levels exceeding the Air Quality Standard upwind of the northeastern New Jersey-New York City metropolitan area on August 10.

The remaining parts of this paper will focus on two areas: the urban plume and large scale advection.

Investigation of Urban Plumes

The high frequency of northwest winds during the study period provided excellent conditions to investigate the previously studied[1-3] urban plumes from the Philadelphia-Wilmington-Camden complex. The complex extends for approximately 30

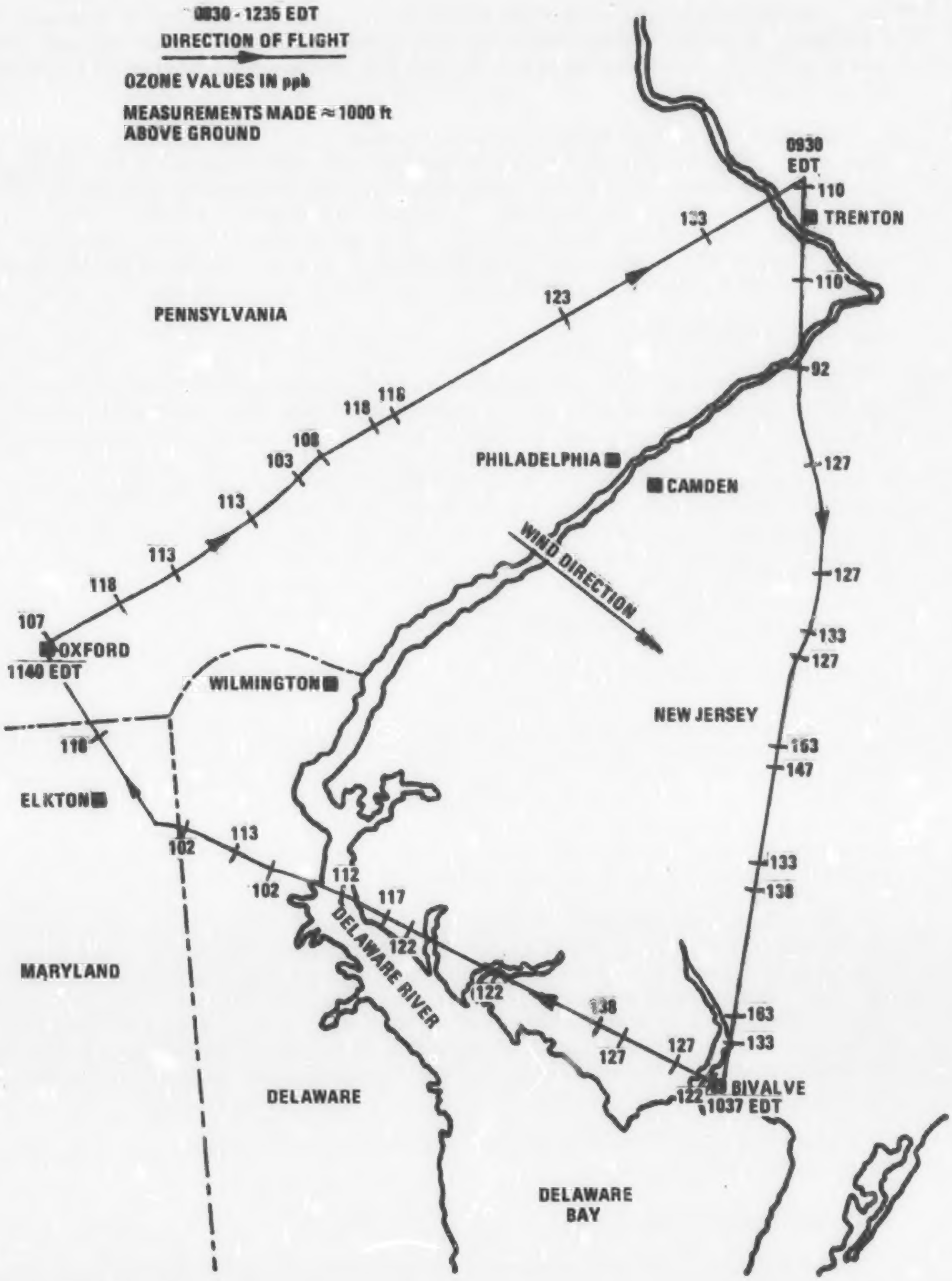

0830 - 1235 EDT
DIRECTION OF FLIGHT
OZONE VALUES IN ppb
MEASUREMENTS MADE ≈ 1000 ft ABOVE GROUND
0930 EDT
110
TRENTON
133
110
123
PENNSYLVANIA
92
116
118
108
103
PHILADELPHIA
CAMDEN
127
113
WIND DIRECTION
113
118
127
107
OXFORD
1140 EDT
133
127
WILMINGTON
NEW JERSEY
116
163
147
ELKTON
113
102
102
133
138
112
117
DELAWARE RIVER
122
MARYLAND
122
138
163
127
127
133
BIVALVE
122
1037 EDT
DELAWARE
DELAWARE BAY

Figure 9-1. Ozone results for southern flight during morning hours of August 10, 1975.

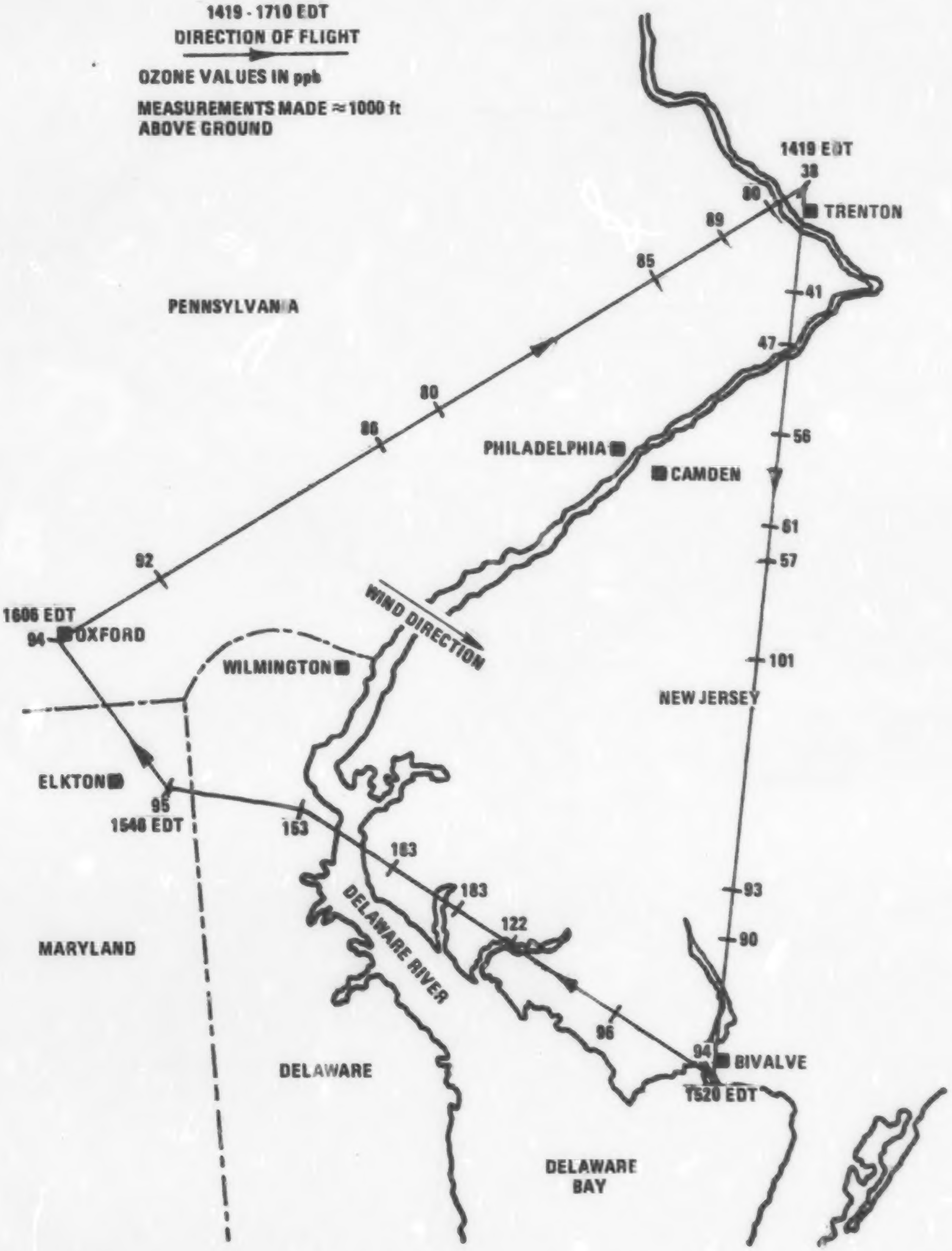

1419 - 1710 EDT
DIRECTION OF FLIGHT
OZONE VALUES IN ppb
MEASUREMENTS MADE ≈1000 ft ABOVE GROUND
1419 EDT
38
TRENTON
80
89
85
PENNSYLVANIA
41
47
80
86
56
PHILADELPHIA
CAMDEN
61
57
92
WIND DIRECTION
1606 EDT
94
OXFORD
WILMINGTON
101
NEW JERSEY
ELKTON
95
1546 EDT
153
163
183
93
122
90
MARYLAND
DELAWARE RIVER
96
94
BIVALVE
1520 EDT
DELAWARE
DELAWARE BAY

Figure 9-2. Ozone results for southern flight during the afternoon hours of August 20, 1975.

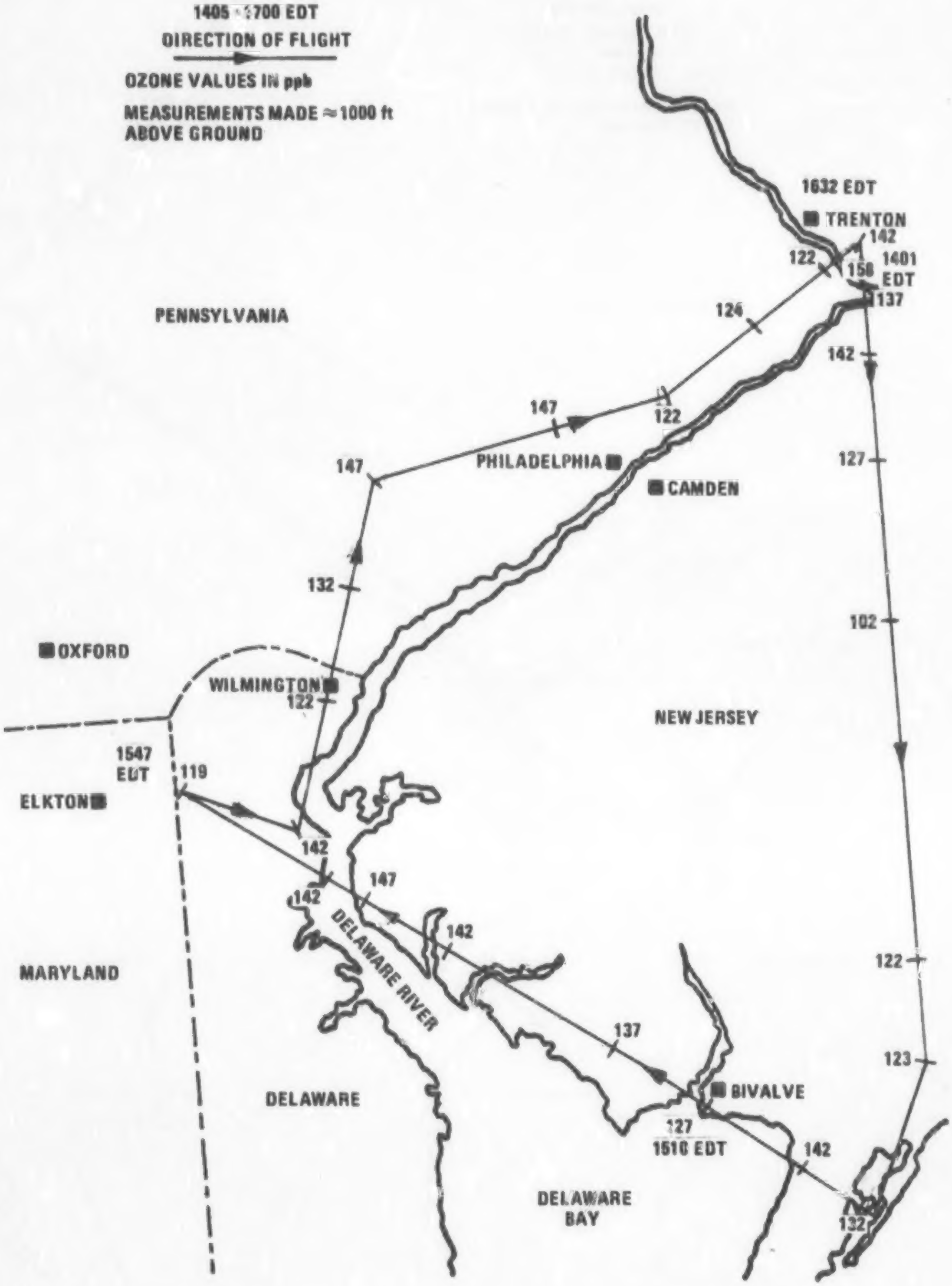

1405 - 1700 EDT
DIRECTION OF FLIGHT
OZONE VALUES IN ppb
MEASUREMENTS MADE ≈ 1000 ft ABOVE GROUND
1632 EDT
TRENTON
142
122
158
1401 EDT
137
PENNSYLVANIA
126
142
147
122
147
PHILADELPHIA
CAMDEN
127
132
102
OXFORD
WILMINGTON
122
NEW JERSEY
1547 EDT
119
ELKTON
142
147
142
DELAWARE RIVER
142
MARYLAND
122
137
123
BIVALVE
DELAWARE
127
1510 EDT
142
DELAWARE BAY
132

Figure 9-3. Ozone results for southern flight during the afternoon hours of August 21, 1975.

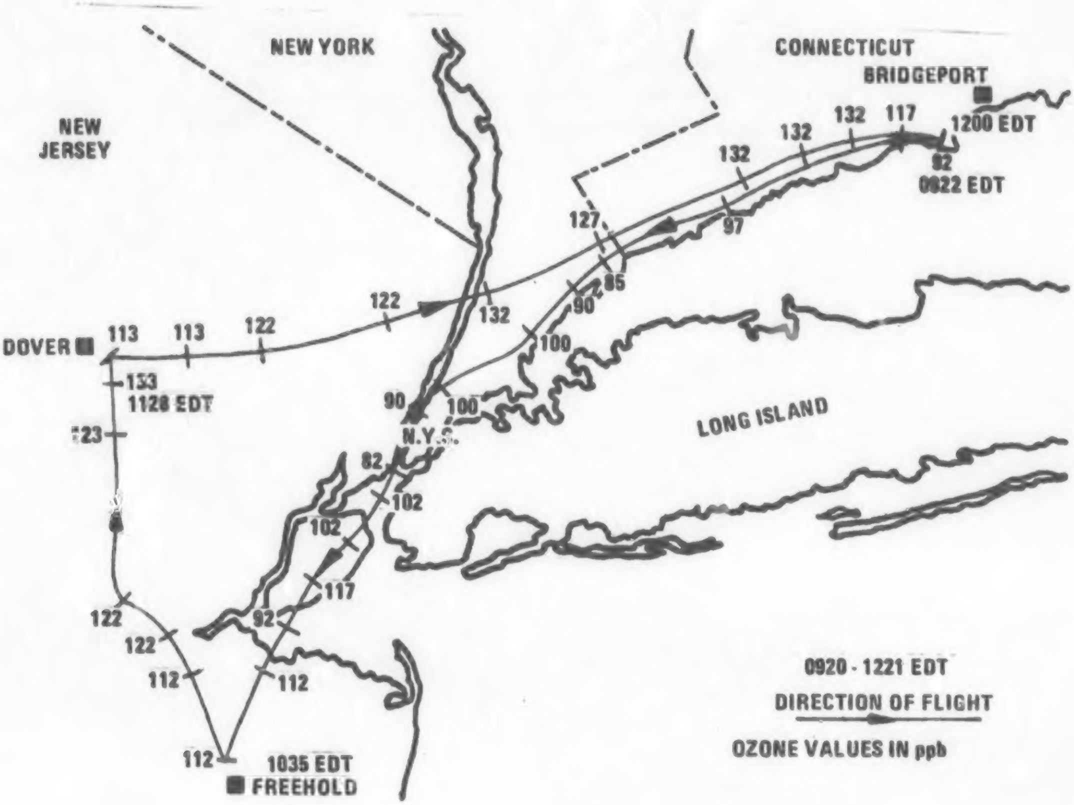

NEW YORK
CONNECTICUT
BRIDGEPORT
NEW JERSEY
132
132
132
117
1200 EDT
92
0922 EDT
127
97
122
132
85
90
100
DOVER
113
113
122
133
1128 EDT
123
90
100
LONG ISLAND
N.Y.C.
82
102
102
117
92
122
122
112
112
112
1035 EDT
FREEHOLD
0920 - 1221 EDT
DIRECTION OF FLIGHT
OZONE VALUES IN ppb

Figure 9-4. Ozone results for northern flight during morning hours of August 10, 1975.

miles on a southwest to northeast line. Consequently, a northwest wind is roughly perpendicular to the source region, and the downwind area has a very low density of manmade sources.

Evidence of an urban plume from this complex was found on August 10 (Figures 9-2 and 9-5) and August 19 (Figure 9-6). During three of these flights (Figures 9-1, 9-5, and 9-6), there appeared to be a plume centerline characterized by an ozone gradient on both sides perpendicular to the centerline. Table 9-1 presents the average upwind concentration and the maximum observed downwind concentration.

For the Philadelphia-Wilmington-Camden complex, the average difference between the average upwind and maximum downwind concentration was 36 ppb, with a range of 16 to 55 ppb. These values are consistent with the difference previously observed. The origin of this urban plume is thought to be a result of a cumulative effect of hydrocarbon and nitrogen oxide emissions in the Philadelphia-Camden-Wilmington complex. Assuming a relatively constant wind direction on the 10th (310° in the morning, 260° in the afternoon), the centerline or downwind ozone maximum can be traced back to south of Philadelphia, just north of Chester, PA. It is suggested that this be investigated further because of the number of oil refineries in this area.

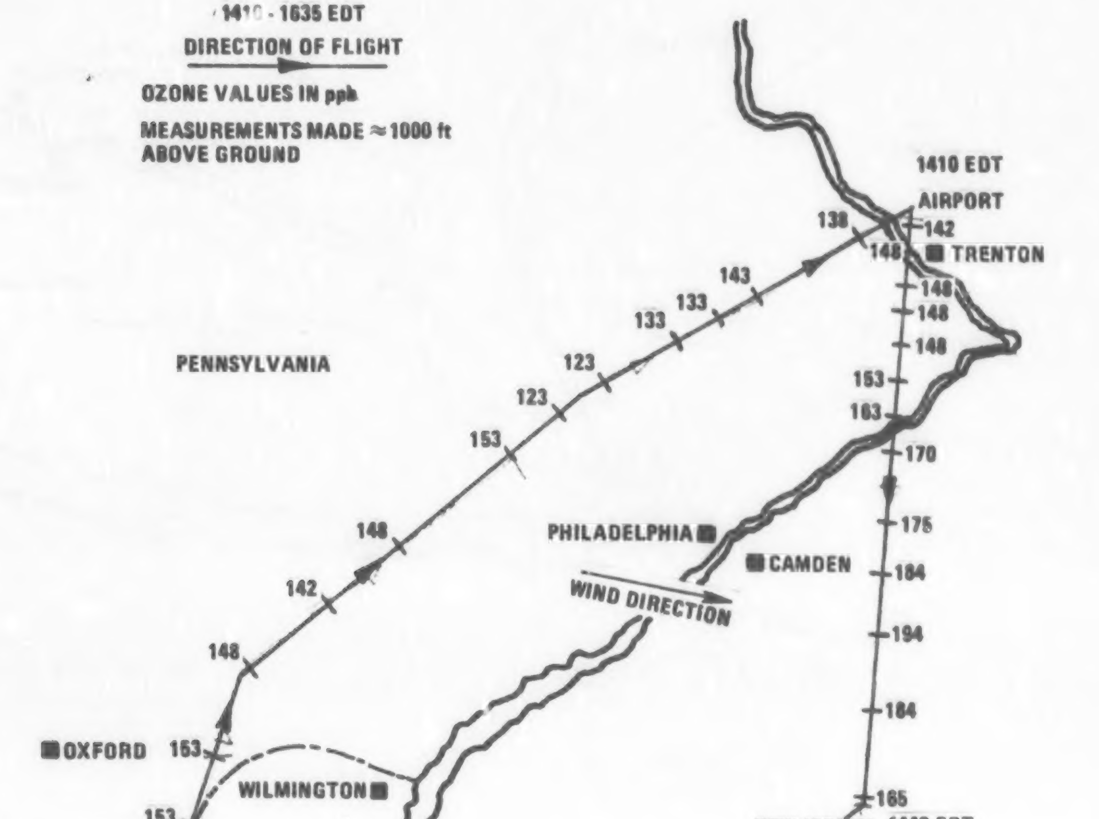

1410 - 1635 EDT
DIRECTION OF FLIGHT
OZONE VALUES IN ppb
MEASUREMENTS MADE ≈ 1000 ft ABOVE GROUND
1410 EDT
AIRPORT
TRENTON
PENNSYLVANIA
PHILADELPHIA
CAMDEN
WIND DIRECTION
OXFORD
WILMINGTON
NEW JERSEY
1442 EDT
1532 EDT
ELKTON
MARYLAND
DELAWARE RIVER
DELAWARE
DELAWARE BAY
BIVALVE
138
148
142
148
148
148
153
163
170
175
184
194
184
165
169
158
158
153
133
133
133
123
133
133
128
153
153
148
142
148
153
123
123
133
133
143

Figure 9-5. Ozone results for southern flight during afternoon hours of August 10, 1975.

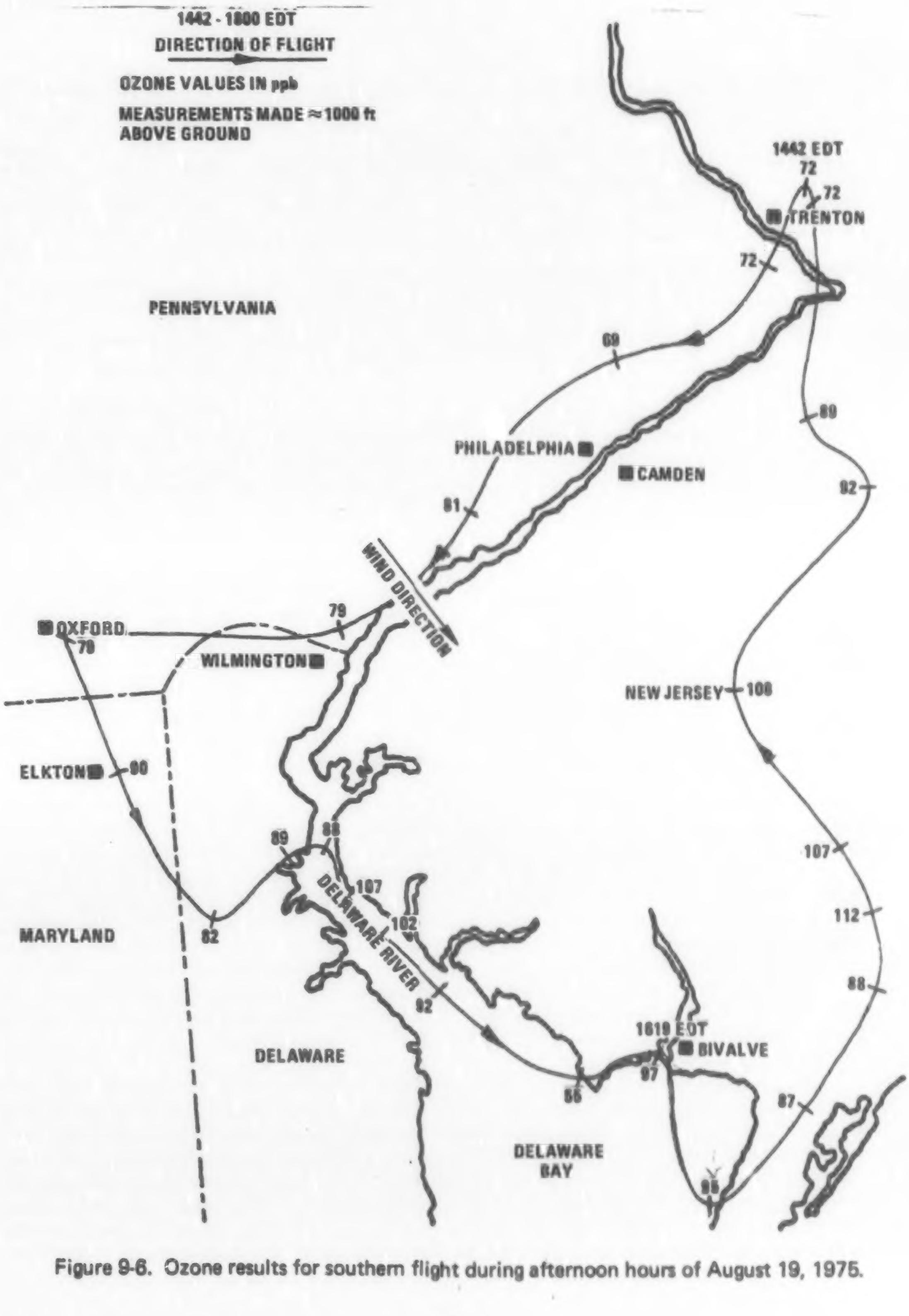

1442 - 1800 EDT
DIRECTION OF FLIGHT
OZONE VALUES IN ppb
MEASUREMENTS MADE ≈ 1000 ft ABOVE GROUND
1442 EDT
72
72
TRENTON
72
PENNSYLVANIA
69
89
PHILADELPHIA
CAMDEN
92
81
WIND DIRECTION
79
OXFORD
79
WILMINGTON
NEW JERSEY
108
ELKTON
90
89
88
107
102
107
112
MARYLAND
82
DELAWARE RIVER
92
88
1619 EDT
BIVALVE
DELAWARE
97
55
87
DELAWARE BAY
95

Figure 9-6. Ozone results for southern flight during afternoon hours of August 19, 1975.

Table 9-1. OBSERVED UPWIND AVERAGE AND DOWNWIND MAXIMUM OZONE CONCENTRATIONS

Date	Time	Urban area	Upwind average concentration, ppb	Downwind maximum concentration, ppb	Δ ppb	Wind	Day	Downwind distance, miles
8/10	a.m.	Phil-Camden	113	153	40	NW	Sunday	27
8/10	p.m.	Phil-Camden	139	194	55	WNW	Sunday	27
8/15	p.m.	NYC	50	128	78	NE	Friday	14
8/19	p.m.	Phil-Camden	78	112	34	NW	Tuesday	50
8/20	p.m.	Phil-Camden	85	102	16	NW	Wednesday	22
8/20	p.m.	Refinery	95	183	88	NW	Wednesday	10
8/20	p.m.	Bridgeport	69	92	20	NNW	Wednesday	29
8/20	p.m.	New Haven	79	142	66	NNW	Wednesday	23
8/20	p.m.	Connecticut	80	95	15	NNW	Wednesday	18

As a result of the observation near Chester, the flight pattern followed on August 20 (Figure 9-2) was modified to include flying downwind of a refinery located in Delaware. It was selected because it was relatively isolated from other nearby hydrocarbon sources and required only a minor modification in the flight pattern. The plume was tracked visibly for about 15 miles. Upwind of the refinery, the ozone concentration was 95 ppb. The downwind concentrations were: 153 ppb at 4 miles, 163 ppb at 10 miles, 183 ppb at 15 miles, and 122 ppb at 25 miles. Between 35 and 40 miles downwind, the ozone concentration was again around 95 ppb.

In the northern sectors of the study, the northeast New Jersey and the New York City area urban plume, which was previously observed,[1,4,5] was also investigated. During August 15 (Figure 9-7), the winds over the area were from the northeast. Ozone concentrations measured at all locations that were not downwind of the New York City-northeast New Jersey area averaged about 60 ppb (except for a few isolated readings near New Haven). Downwind in the vicinity of New Brunswick, NJ, the ozone reached 97 ppb, with a well-defined gradient perpendicular to the wind direction. Three hours later, the ozone over New Brunswick was 117 ppb, while a maximum concentration of 123 ppb was observed 15 miles to the southwest near Princeton. At the time, upwind of New York City over Bridgeport, CN, the observed ozone values were only about 50 ppb.

As previously mentioned, because of the presence of northwest winds, a special flight was conducted in the northern part of the study region on August 20 to investigate the transport of ozone from Connecticut to Long Island (Figure 9-8). Several observations were made on this flight. First, it appears that there is a Connecticut plume. This is manifested by the ozone values over the north shore of Long Island being higher (by an average of 17 ppb) than over the southern shore of Connecticut. Since precursor emissions over the Sound should be negligible, it is reasonable to attribute this increase to emissions in Connecticut. The ozone value over New Haven was 79 ppb. Directly downwind on the north shore of Long Island, the ozone reached

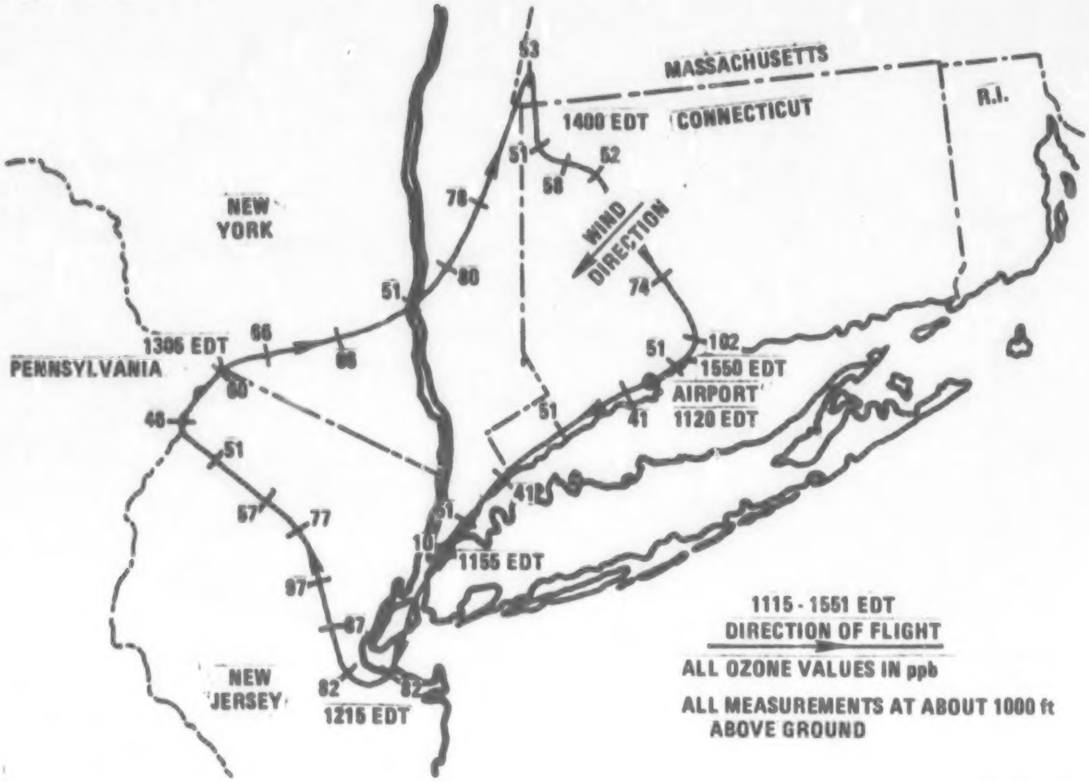

MASSACHUSETTS
R.I.
1400 EDT
CONNECTICUT
53
51
52
58
78
NEW YORK
WIND DIRECTION
74
80
51
1305 EDT
66
PENNSYLVANIA
66
80
51
102
1550 EDT
AIRPORT
1120 EDT
51
41
46
51
41
57
77
51
10
1155 EDT
97
87
NEW JERSEY
82
82
1215 EDT
1115 - 1551 EDT
DIRECTION OF FLIGHT
ALL OZONE VALUES IN ppb
ALL MEASUREMENTS AT ABOUT 1000 ft ABOVE GROUND

Figure 9-7. Ozone results for northern flight during afternoon hours of August 15, 1975.

152 ppb. This supports the concept of ozone generation in transit from Connecticut into Long Island (also See Figure 9-9a).

The difference between the upwind and the downwind ozone concentrations within the urban plume are evidence of ozone synthesis from urban sources.[5] This can also be supported by examining the vertical profiles. The ozone values at the 2000-foot level will be used below as a point of reference. This level is generally within the haze layer and above the level at which ground level NO sources cause a depression in the ozone values.

On August 10, the winds were out of the northwest in the morning and shifted to the west-southwest in the afternoon. On westerly winds, Trenton and New Brunswick, NJ, would be free from influence by either of the two metropolitan areas. Figures 9-9B and 9-9C illustrate that the morning and afternoon ozone profiles for New Brunswick and Trenton are very similar, with only a slight increase in ozone concentrations. The downwind sites, however, all show marked increases. At the 2000-foot level, a 64 ppb increase was observed over Bridgeport (Figure 9-9D), 74 ppb over Mamaroneck (Figure 9-9E), and 41 ppb over Ancora, (Figure 9-9F).

On August 19, northwest winds persisted throughout the day. The upwind sites were Trenton, New Brunswick, Dover, and Bridgeport, while Bivalve was downwind

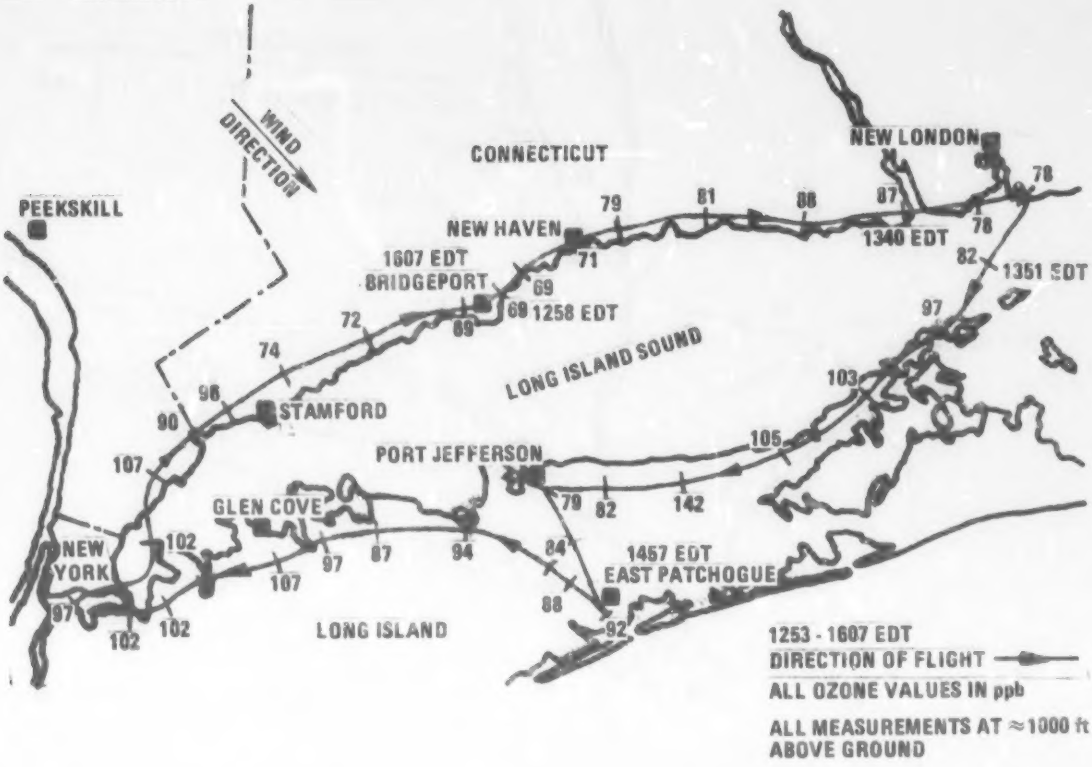
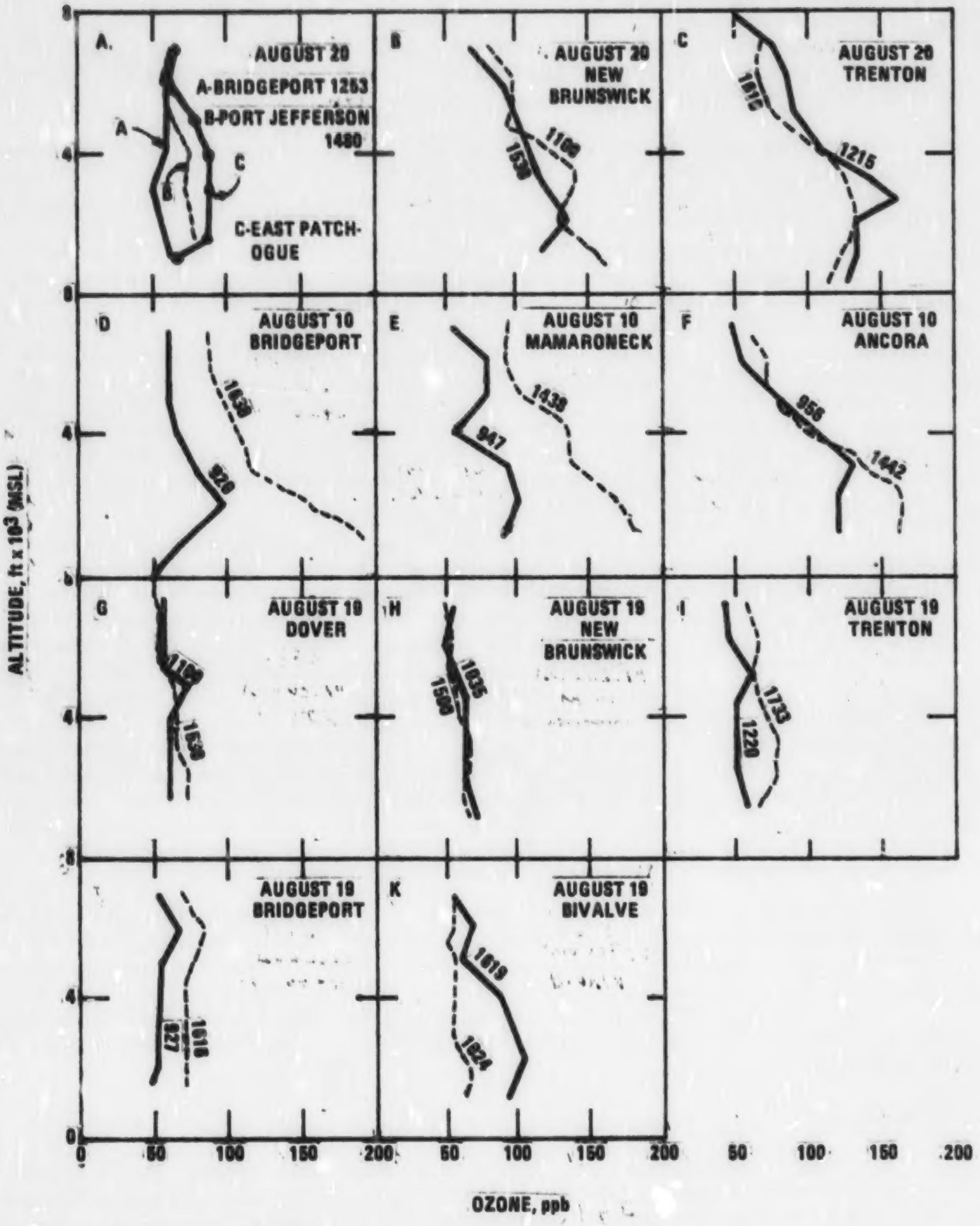

WIND DIRECTION
CONNECTICUT
PEEKSKILL
NEW LONDON
78
87
88
81
79
NEW HAVEN
1340 EDT
78
71
82
1351 EDT
1607 EDT
BRIDGEPORT
69
69 1258 EDT
89
72
97
74
LONG ISLAND SOUND
103
98
STAMFORD
90
107
PORT JEFFERSON
105
79
82
142
GLEN COVE
NEW YORK
102
97
87
94
84
1457 EDT
EAST PATCHOGUE
107
88
97
102
102
LONG ISLAND
92
1253 - 1607 EDT
DIRECTION OF FLIGHT
ALL OZONE VALUES IN ppb
ALL MEASUREMENTS AT ≈1000 ft ABOVE GROUND

Figure 9-8. Ozone results for northern flight during afternoon hours of August 20, 1975.

of the Philadelphia-Wilmington complex. Vertical profiles completed at New Brunswick and Dover (Figures 9-9G and 9-9H) show little evidence of ozone synthesis or transport. The larger upwind urban areas, Trenton and Bridgeport, show increases of 28 and 35 ppb, respectively. It seems reasonable that the increases are due primarily to relatively local sources of precursors, since they are not downwind of any major urban area. At 2000 feet, the ozone concentration at Bivalve (Figure 9-9K) increased 38 ppb between 1024 and 1619 EDT. This could be attributed to transport from the Philadelphia-Wilmington-Camden complex since the area between the urban complex and the site is rural.

With northwest winds, similar observations were made over Trenton on August 20. At the 2000-foot level, the ozone increased 28 ppb. This supports the observations discussed in the preceeding paragraph.

On August 15, verticals were made over Trenton, Bivalve, and Elkton before sunrise and in the early afternoon. It is interesting to note that during all the verticals before sunrise, ozone levels in excess of 80 ppb were observed except over Trenton. In the afternoon, the ozone at the 2000-foot level at Trenton increased an additional 45 ppb. Since the winds were from the northeast, it appears some of this increase was due to transport from the New York metropolitan area. The Bivalve and Elkton verticals show no evidence of ozone synthesis, but this may have been partially due to a thickening cloud cover that moved in from the south in the afternoon.



Figures 9-9a through 9-9k. Vertical profiles for ozone at serveral sampling sites at various sampling times for August 10, 19, and 20, 1975.

Large-Scale Ozone Advection

Since the highest ozone values observed in the northeast generally occur on southwest winds, it was important that this condition be investigated. Southwest winds occurred during the afternoon of August 21.

On the afternoon of August 20, with light north-northwest winds prevailing, ozone values were relatively low over the region with two exceptions: parts of Long Island and New York City, and the extreme southern portion of the southern flight area (see Figures 9-8 and 9-2). On the morning of the 21st, these high concentrations continued to persist over the extreme southern portion (Figure 9-10) but not over the New York City area (Figure 9-11). South of Philadelphia, the ozone concentrations ranged from 107 to 122 ppb, while north of Philadelphia extending into Connecticut, it ranged from 20 to 70 ppb. Winds overnight and into the morning were light and variable (<3 mph). Consequently, very little transport could occur. Between 1100 and 1200, the winds shifted and a very strong south-southwest flow was established over the region from the surface to 3000 feet. During the afternoon, the skies over the region were partly cloudy (ranging from 30 to 60 percent cloud cover) and hazy sunshine persisted. As a result, the meteorological conditions were conducive for ozone synthesis and transport. The dramatic changes in the meteorological conditions that occurred during the day are illustrated in Table 9-2.

As the wind shifted, it appeared that the air containing the high ozone over the southern part of the region moved rapidly northeastward through the New York City area around 1430 to 1500 EDT, (Figures 9-12 and 9-3). Since the wind shift at Philadelphia occurred around 1100 EDT, the air south of Philadelphia would have to travel about 80 miles in 3.5 to 4 hours (20 to 25 mph). Table 9-2 indicates that conditions were conducive for such rapid transport. Surface observations of ozone levels also supported rapid transport. At Ancora, located in southern New Jersey, the ozone rose rapidly between 1100 and 1200 EDT from 29 to 67 ppb and reached its maximum of 101 ppb between 1200 and 1300 EDT. Further north in New Jersey, Bayonne reached 73 ppb between 1300 and 1400 EDT and the ozone continued to rise until 1800 hours when it reached 100 ppb. Traveling further northeastward, Stamford, CN, reached 60 ppb at 1400 EDT and 90 ppb by 1500 EDT. In New Haven, CN, the ozone levels did not reach 70 ppb until 1700 EDT. All these sites demonstrated rapid increases in ozone, but most significant was the time at which it occurred.

The high levels of ozone over Connecticut (about 180 ppb) cannot be attributed solely to transport from the southern New Jersey-Delaware area because the maximum concentrations observed in the southern area on the afternoon of the 20th and the morning of the 21st were on the order of 120 ppb. This is excluding the very localized higher values observed downwind of the refinery plume. It is reasonable to assume that at least 60 ppb of ozone was synthesized in route from extreme southern New Jersey to Connecticut.

SUMMARY

1. With one exception, i.e., downwind in the urban plume, ozone appeared to be uniformly distributed over the study area, which included: extreme northeastern Maryland, northern Delaware, southeastern Pennsylvania, New Jersey, the New York City metropolitan area, and southeastern Connecticut, on most of the days examined.

2. There was evidence of an urban plume emanating from Philadelphia-Camden-Wilmington metropolitan area, the northeastern New Jersey-New York City-southeastern Connecticut metropolitan area, and New Haven, CN.

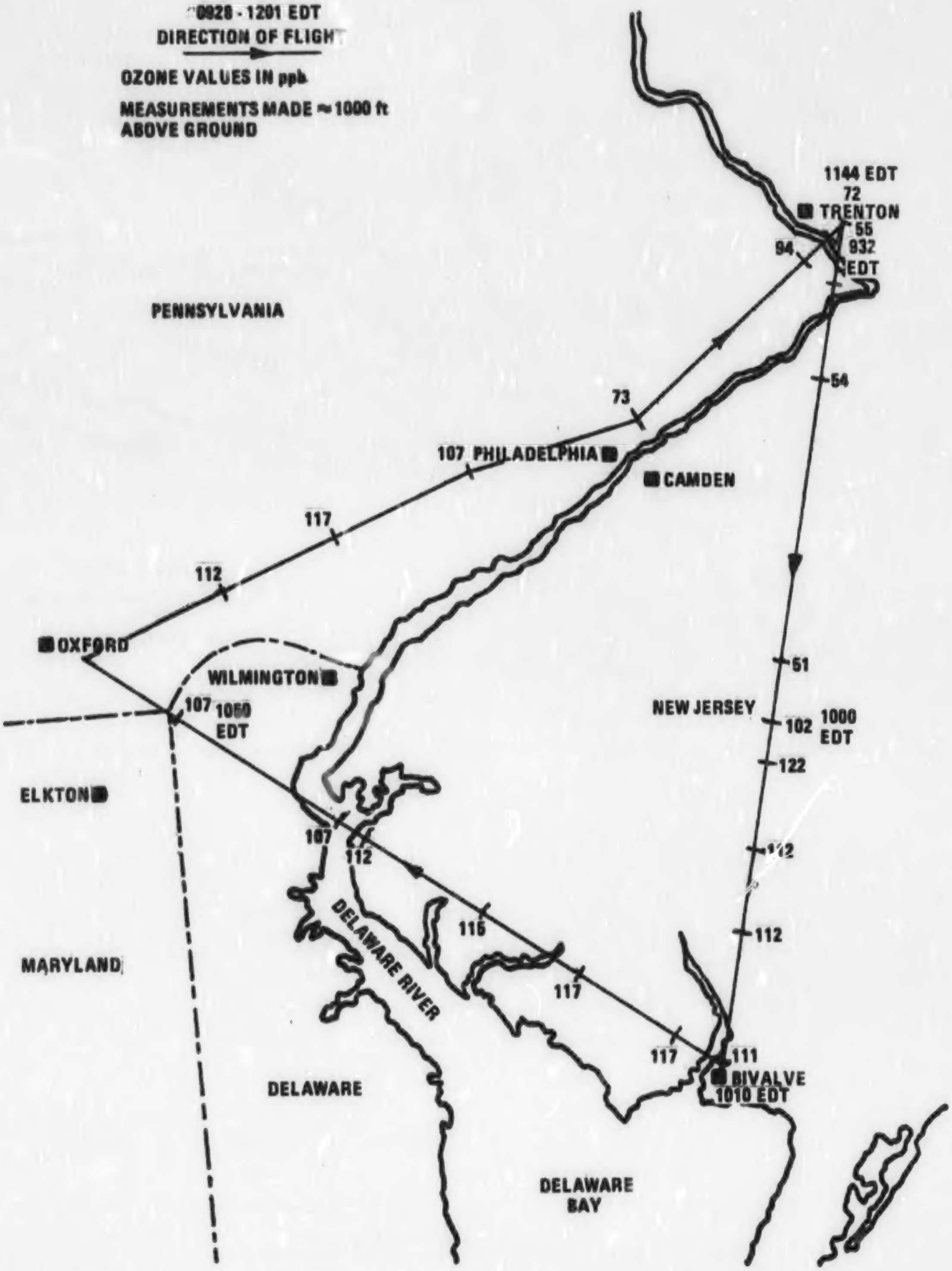

0928 - 1201 EDT
DIRECTION OF FLIGHT
OZONE VALUES IN ppb
MEASUREMENTS MADE ≈ 1000 ft ABOVE GROUND
1144 EDT
72
TRENTON
55
932
EDT
94
PENNSYLVANIA
54
73
107
PHILADELPHIA
CAMDEN
117
112
OXFORD
WILMINGTON
107
1050
EDT
51
NEW JERSEY
102
1000
EDT
122
ELKTON
107
112
112
115
DELAWARE RIVER
112
MARYLAND
117
117
111
BIVALVE
1010 EDT
DELAWARE
DELAWARE BAY

Figure 9-10. Ozone results for the southern flight during morning hours of August 21, 1975.

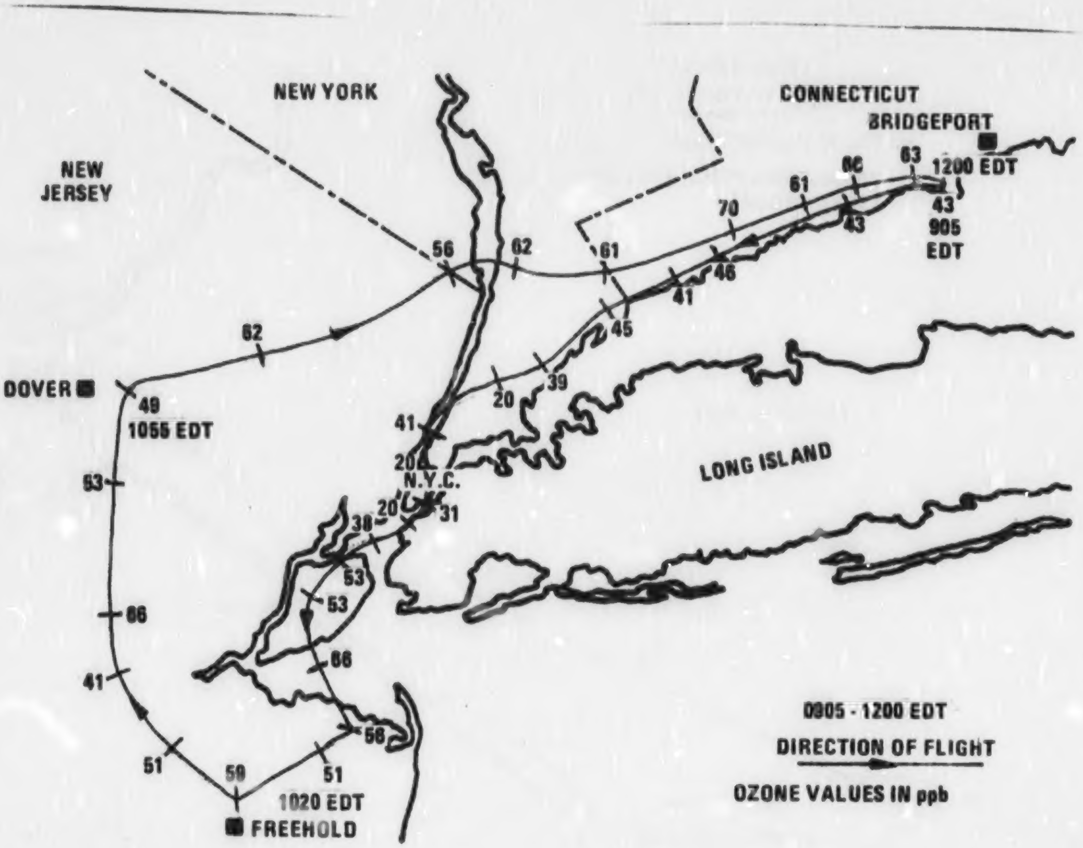

NEW YORK
CONNECTICUT
BRIDGEPORT
NEW JERSEY
1200 EDT
905 EDT
DOVER
1055 EDT
N.Y.C.
LONG ISLAND
1020 EDT
FREEHOLD
0905 - 1200 EDT
DIRECTION OF FLIGHT
OZONE VALUES IN ppb
56
62
61
70
61
66
63
43
43
46
41
45
62
49
20
39
41
20
53
38
20
31
53
53
66
66
41
51
59
51
68

Figure 9-11. Ozone results for northern flight during morning hours of August 21, 1975.

Table 9-2. METEOROLOGICAL CONDITIONS, 1000 AND 2000 EDT, FORT TOTTEN, NEW YORK, AUGUST 21, 1975

	Wind speed (mph) and direction	
Altitude, ft	1000 EDT	2000 EDT
SFC	NE 60° @ 8	SSW @ 26
2000		@ 39
3000	NW 290° @ 7	SW @ 48
4000		@ 47
5000		WSW @ 50
6000	NNW 300° @ 18	

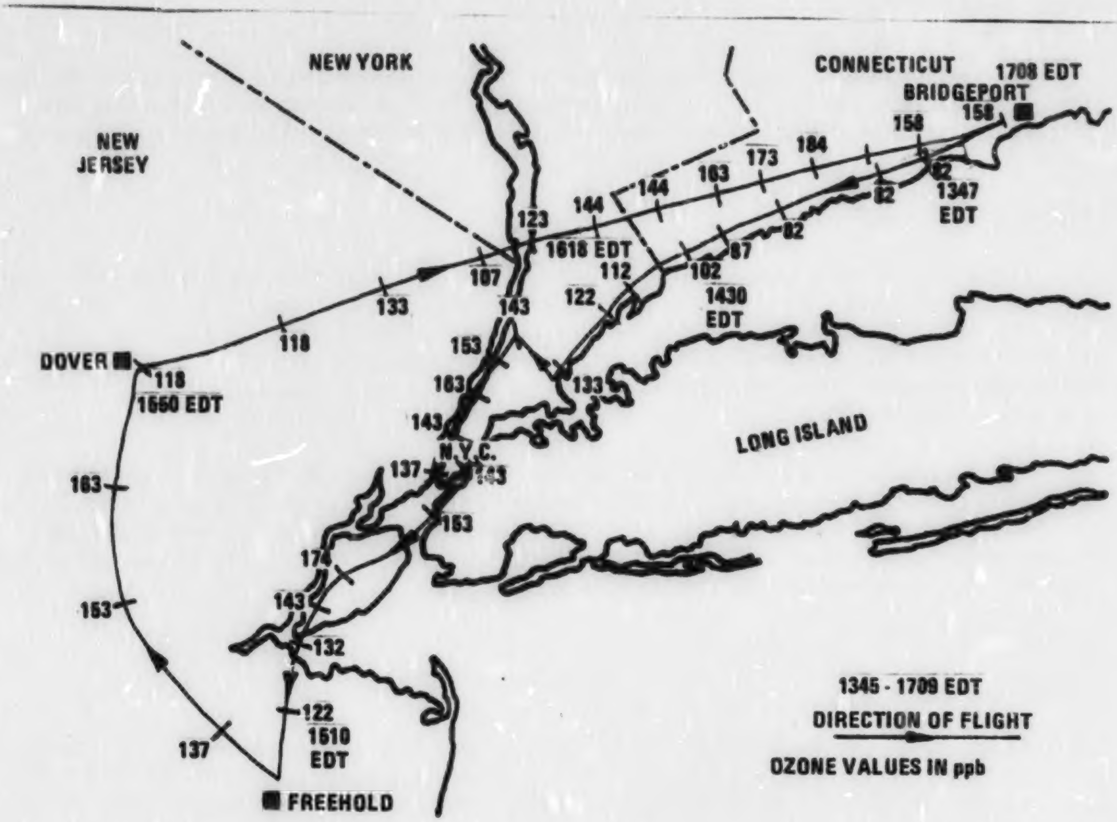

NEW YORK
CONNECTICUT
1708 EDT
BRIDGEPORT
NEW JERSEY
158
158
184
173
163
144
144
123
1618 EDT
82
1347 EDT
82
82
87
112
102
1430 EDT
107
133
143
122
118
DOVER
118
1550 EDT
153
163
133
LONG ISLAND
143
N.Y.C.
137
143
163
153
174
153
143
132
122
1510 EDT
137
FREEHOLD
1345 - 1709 EDT
DIRECTION OF FLIGHT
OZONE VALUES IN ppb

Figure 9-12. Ozone results for northern flight during afternoon hours of August 21, 1975.

3. The maximum increases in the ozone observed within Philadelphia-Camden-Wilmington and northeastern New Jersey-New York City-southeastern Connecticut urban plumes were 55 ppb and 78 ppb, respectively.

4. Large-scale advection of ozone was observed on August 21 from Delaware to Connecticut, a distance of approximately 180 miles.

5. Ozone synthesis was observed as an air mass traveled from southern Connecticut over the Long Island Sound to Long Island. The net generation was on the order of 15 to 20 ppb.

6. There is evidence of significant ozone generation downwind of oil refineries.

7. There is some evidence, which needs to be investigated further, that much of the ozone observed in the Philadelphia-Camden-Wilmington urban plume may originate just to the south of Philadelphia rather than in the center of the city. This area contains several large refinery complexes.

8. The data support past conclusions that the air mass entering New Jersey and in New Jersey-New York-Connecticut Air Quality Control Region from a westerly direction frequently contains ozone concentrations exceeding the National Ambient Air Quality Standard.

9. The extremely high ozone levels previously recorded in Connecticut did not occur during the study period. Consequently, it is recommended that additional flights be conducted during the earlier part of the summer when such episodes are more frequent.

ACKNOWLEDGEMENTS

The authors wish to express our gratitude to the following people for their support in this project: Vincent Krushak (New Jersey Department of Environmental Protection) and Thomas Peters and Michael Anderson (Connecticut Department of Environmental Protection) for conducting many of the flights, and Richard Taylor (New York State Department of Environmental Conservation) for his assistance in interpreting the meteorological data.

We extend our appreciation also to Robert Witby (New York State Department of Environmental Conservation) and William Ormand (New Jersey Department of Environmental Protection) for their analyses of the hydrocarbon samples, and to Konrad Wisniewski (Interstate Sanitation Commission) for conducting many of the experiments and for coordinating the quality assurance program.

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10. AIR QUALITY ABOVE THE MORNING SURFACE INVERSION AND ITS EFFECT ON URBAN OZONE CONCENTRATION

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INTRODUCTION

In 1973 and 1974, Drs. William Stasiuk and Peter Coffey discovered that New York rural air monitoring stations exhibited violations of the National Ambient Air Quality Standard for ozone as frequently as urban stations, although the urban stations had higher maximum values during mid- to late-afternoon periods. Rural stations separated by distances of 300 miles showed remarkably similar patterns; ozone concentration increased as high pressure systems entered the region and decreased as the systems moved away. Urban levels showed the typical diurnal variation, with maximums following the general rural pattern associated with high pressure cells. Rural levels were found to have little diurnal variation. Transport of ozone and/or precursors could not explain such events; thus, we considered a significant proportion of the ozone observed to be a regional air mass characteristic. Since there were often widespread ozone levels in excess of the standard, the air mass levels alone were considered to contribute significantly to the typical urban diurnal pattern through a mixing and transport mechanism. To test this hypothesis and to provide greater understanding of ozone variations, a study of air quality above the urban nocturnal inversion was undertaken. The objectives of this study were:

1. Establishment of a high altitude urban monitoring site.
2. Measurement of ozone above and below the low level nocturnal inversion.
3. Measurement of nitrogen oxides and hydrocarbons associated with ozone levels.
4. Measurement of regional ozone and vertical ozone profiles by instrumented aircraft flights.

The high altitude urban site was located at the 82nd floor of World Trade Center II (308 meters), while a ground level station was located at Roosevelt Island. The low level nocturnal inversions were found to occur both above and below the World Trade Center site level. Instrumented aircraft flights were made on 8 days in June, the 17th through 24th. Other state agencies provided hourly ozone data for the mid-Atlantic States region in order to plot regional ozone isopleth maps. Data from 95 individual stations were utilized.

WORLD TRADE CENTER SITE

Ozone, NO, and NO_2 were monitored continuously from June through September 1975 at the 82nd floor (308 meters) of the World Trade Center (WTC), Tower II, in New York City (Figure 10-1). Sample was drawn by the instrument through a 1/4-

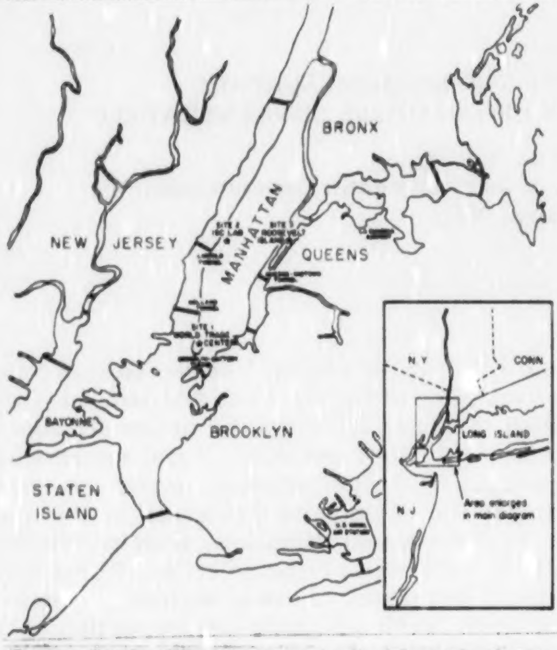

Figure 10-1. Sampling sites in the New York City area.

inch O.D. Teflon sample line that extended horizontally from the building a distance of 10 feet and was supported in an aluminum conduit. A single instrument, an Aero-chem Chemiluminescence Analyzer, was used to monitor all three species. Fire laws prohibited the use of ethylene chemiluminescence monitors. During August, an acoustic sounder was employed at nearby Roosevelt Island to measure low level nocturnal inversions.

O_3, NO, and NO_x data for the period August 8-12, typical of the study period, are presented in Figure 10-2. Wind directions for the period were generally west to north-northwest as the region was under the influence of a modified summertime polar air mass that had developed over the southern Canadian Rockies on August 4 and moved east-southeastward across the United States into the southeastern states by August 12. During August 6, 7, and 8, cloudiness and rainy periods covered the sample area. This was a period of low ozone throughout the mid-Atlantic region. By the 9th, high pressure was established over the eastern third of the country. At this time, the ozone increased markedly and remained elevated until the high moved into the deep south. The high pressure system appeared to have greater effect on the ozone levels than the morning inputs of NO. NO did exhibit scavenging effects on ozone, but the NO_x-O_3 interrelationships are difficult to assess due to continuous inputs, atmospheric mixing, and advection.

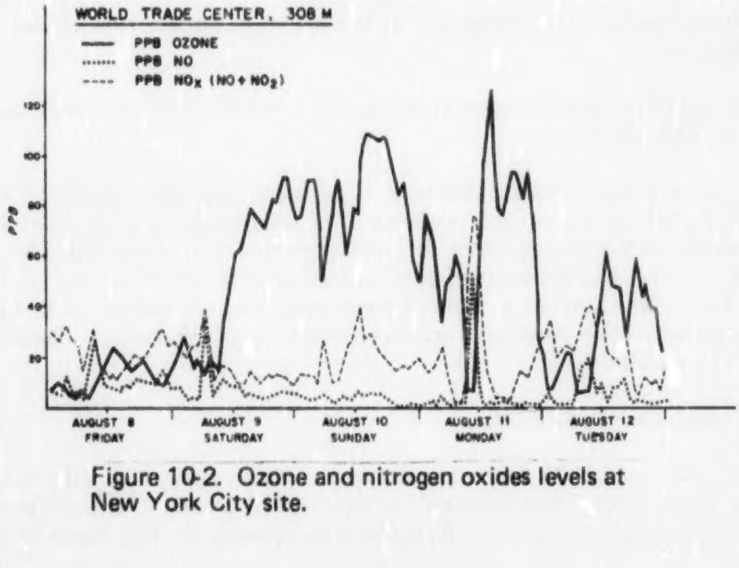

Figure 10-2. Ozone and nitrogen oxides levels at New York City site.

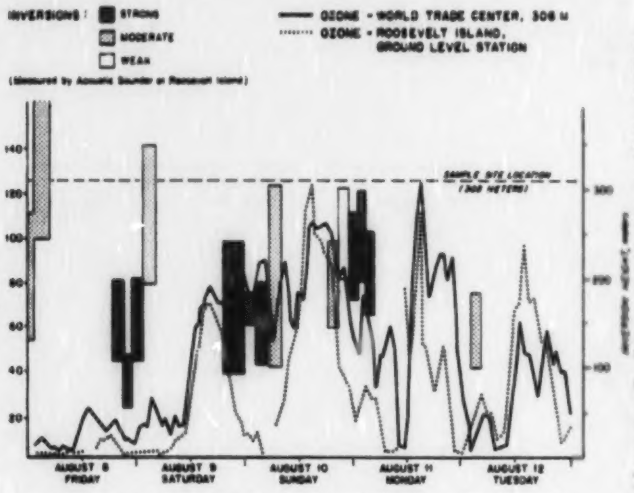

Figure 10-3. Ozone and inversion data (measured by acoustic sounder) at World Trade Center and Roosevelt Island.

Ozone was also monitored at the Roosevelt Island ground level station 7.2 miles northeast of the WTC (see Figure 10-1). The data presented in Figure 10-3 show three well developed nocturnal inversions below the 308-meters level of the WTC site. During the inversion of August 9-10, the O_3 levels observed at the WTC site were much higher than at the ground site. Additionally, the highest O_3 values occur near midnight, a result quite similar to previous observations at ground level rural stations in New York State. Somewhat the same results were observed for the inversion condition of August 10-11.

On August 8-9, the O_3 levels were low both above and below the nocturnal inversion. As previously stated, the period of August 6-8 was one of low regional O_3; thus, the air layer observed above would be expected to be low in ozone.

The data indicate that the air layer above the nocturnal inversion exhibits characteristics associated with ozone levels observed at ground level rural stations in New York State; it appears fairly representative of background ozone levels plus any accumulation of ozone from photochemical processes during the day. When separated from ozone scavengers by the nocturnal inversion, the upper air layer retains a relatively high O_3 content which, following the breakup of the inversion, will mix with ozone-depleted air near the surface and contribute to the typically observed increase in ozone through the day at surface sites.

INSTRUMENTED AIRCRAFT STUDIES

Instrumented helicopter flights over the New York-New Jersey area between Trenton and New York City were made on 8 days in June, the 17th through 24th. A New York State government helicopter was instrumented with an AID portable ozone monitor calibrated by the Interstate Sanitation Commission (NBS calibration) and provided with altitude correction data by the manufacturer. A 5-foot length of Teflon tubing extended from the helicopter through the door seal. Ground and air tests with various lengths of tubing indicated the system used was not affected by aircraft exhaust or rotor wash.

The flight of June 23 was considered representative of a high ozone situation, and flight data are presented in Figures 10-4 to 10-7. Figure 10-4 is a map of the NJ-NYC region with flight path, altitudes (feet), times (EDT), and ozone levels (ppb) indicated. The meteorological conditions were those typically favoring high ozone level development in this region: a high pressure system was located off the mid-Atlantic coast; surface winds were southwest at 11 knots; 1000- to 2000-foot winds were west-southwest at 24 knots; 3000- to 10,000-foot winds were west-northwest at 10 knots;

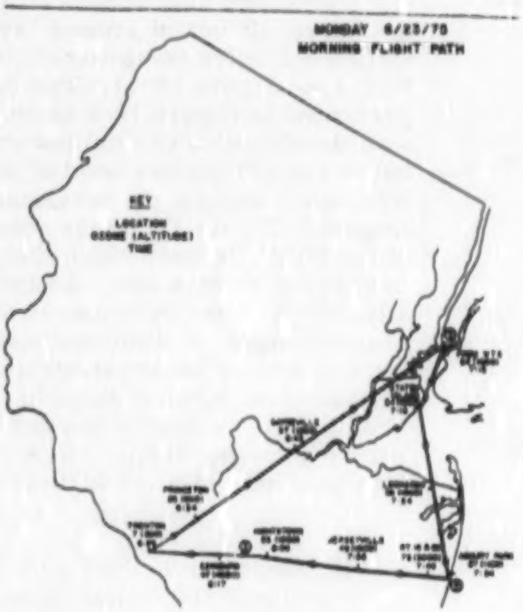
MONDAY 6/23/75
MORNING FLIGHT PATH
KEY
LOCATION
OZONE (ALTITUDE)
TIME

Figure 10-4. Flight pattern and ozone results (in ppb) for morning flight of June 23, 1975.

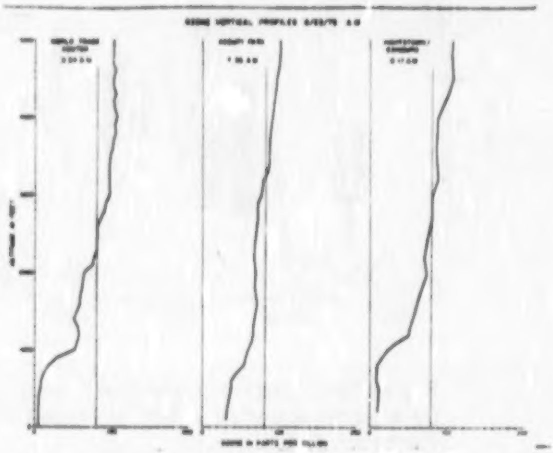

Figure 10-5. Vertical ozone profiles at three locations measured during morning flight of June 23, 1975 (Figure 10-4).

there were early morning low level inversions (data from Fort Totten) at surface to 200 meters and 419 to 910 meters. There was a subsidence inversion based at 1817 meters with a top of 2149 meters, which lowered to the 1500-meter level during the afternoon.

During the morning flight (Figure 10-4), O_3 levels increased with altitude from 7 ppb at the surface at Trenton to about 55 ppb at the 1000-foot level. A vertical to

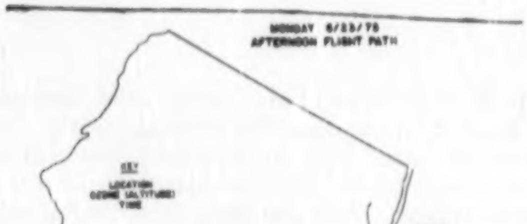
MONDAY 6/23/75
AFTERNOON FLIGHT PATH
KEY
LOCATION
OZONE (ALTITUDE)
TIME

Figure 10-6. Flight pattern and ozone results (in ppb) for afternoon flight of June 23, 1975.

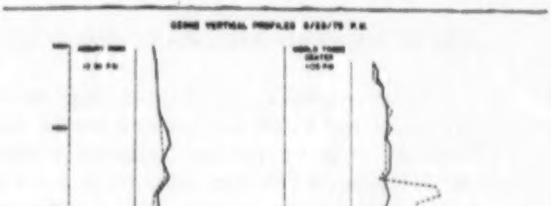

Figure 10-7. Vertical ozone profiles at two locations measured during afternoon flight of June 23, 1975.

5000 feet was made at the WTC. Ozone levels remained at about 55 ppb on the third leg at 1000 feet. Another vertical was performed at Asbury Park. On the southerly third leg at 1000 feet the ozone remained at the 55-ppb level, but was much higher (75 to 97 ppb) at 3000 and 4000 feet. A third vertical was made at Hightstown.

The verticals showed reduced levels of ozone below the morning inversion heights at all three locations (Figure 10-5). Ozone was 70 to 100 ppb from 2000 to 4000 feet and 100 to 110 ppb from 4000 to 5000 feet. The profiles were similar at WTC and Hightstown, while levels below 1000 feet were slightly higher at Asbury Park, quite probably reflecting a lower amount of ozone scavenging due to less local pollution.

Figure 10-6 presents the afternoon flight path for June 23. The flight path was reversed in direction from that of the same morning and a 3-hour stop at LaGuardia Airport was required. Vertical ozone profiles were obtained at Asbury Park and the WTC. Winds during the flight remained from the southwest. Ozone levels on the southern leg had increased from about 55 ppb during the morning to 90 to 133 ppb at 1000 feet. Increasing levels of ozone were encountered approaching New York City from the southwest. During the return flight in the late afternoon, values of approximately 200 ppb were observed over central New Jersey.

Of particular interest are the afternoon profiles at Asbury Park and the WTC shown in Figure 10-7. The former shows a nearly constant concentration of ozone with altitude (105 to 115 ppb). This concentration is virtually the same as the region-wide ozone concentration at 4000 to 5000 feet during the morning flight. The lack of large scale sources of scavengers in the Asbury Park area and a well developed sea breeze result in a uniform mixing of ozone from aloft with low ozone destruction. This is possibly the best approximation of the regional background ozone concentration. This does not necessarily mean "natural" background ozone; the various sources of this regional background level are a matter of debate and require further investigation. Above 3000 feet, the WTC profile is in good agreement with the regional background concentration (110 to 120 ppb), but is significantly higher (180 to 200 ppb) below 3300 feet. It should be noted that, except for Staten Island, the WTC was upwind of New York City hydrocarbon and NO_x sources and the air entering the New York City area had a measured ozone concentration of 150 ppb. This indicates that precursors to the southwest of New York City are being emitted and photochemically reacting to produce O_3, which subsequently is advected into New York City. Thus, New York City can suffer from photochemical pollution not of its own making as well as generate ozone precursors that may cause further ozone pollution downwind. The contribution of sources upwind of New York City should be considered when assessing the impact of New York City sources on receptors downwind.

OZONE ISOPLETH MAPS

Figures 10-8 to 10-11 map the surface ozone conditions for the day of the flight over the mid-Atlantic states. The maps were plotted from data submitted by 95 monitoring stations (Figure 10-12 and Table 10-1). Wind directions at the surface and above 5000 feet are indicated on the maps for the New York City area. The maps indicate the very widespread nature of high ozone levels, indicating a regional problem. Some very high centers develop and grow throughout the day; however, this effect appears to be superimposed upon the regional phenomenon.

The isopleth maps and flight data for the entire study period indicate a general increase near the surface during the morning over a wide region and a further increase during the day, particularly downwind of urban areas. A combination of local

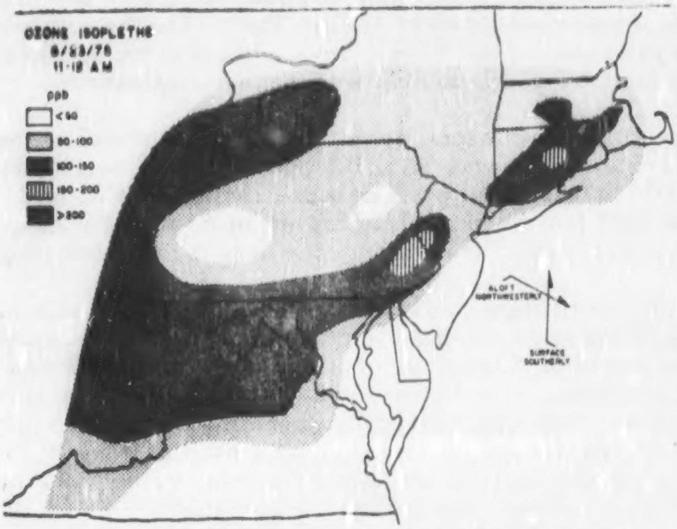
OZONE ISOPLETHS
6/23/75
11-12 AM
ppb
<50
50-100
100-150
150-200
>200
ALOFT NORTHWESTERLY
SURFACE SOUTHERLY

Figure 10-8. Ozone isopleths for 1100-1200 time period of June 23, 1975, constructed using data from a network of 95 ground-based sampling stations.

O_3 generation and destruction, mixing of ozone-rich air from aloft with ozone-depleted air at the surface, and advection appear to be producing the levels and patterns of ozone observed at ground level.

HYDROCARBON-OXIDANT STUDIES

Ambient hydrocarbons in the C_2-C_6 range were measured by gas chromatographic techniques at the WTC (308-meter altitude) and Interstate Sanitation Commission Laboratories (ISC), fourth floor, W. 48th, Manhattan. Approximately 75 integrated 3-hour samples were collected in 5-liter Tedlar bags over the period June 20 through August 20. During the period July 7-18, an intensive sampling program was undertaken on weekdays. Samples were collected by an automated system at 0530 to 0830 hours and 1230 to 1530 hours at the WTC and ISC sites. The early sample was not available on Mondays and three ISC samples were missing for the period. Analysis was made by cryogenic trapping of hydrocarbons from a 70-cm^3 aliquot of the ambient sample. The concentrated sample was injected to the GC column (2 feet x 1/16-inch. O.D. activated alumina), which was temperature programmed from 20°C to 200°C. Figures 10-13 and 10-14 present representative calibration and ambient chromatograms.

Individual hydrocarbons were grouped as C_3-C_6 paraffins, C_2-C_6 olefins, and acetylene and plotted for each site in Figure 10-15A. The data points represent 3-hour integrated averages and the graph is, thus, not intended to present a continuous

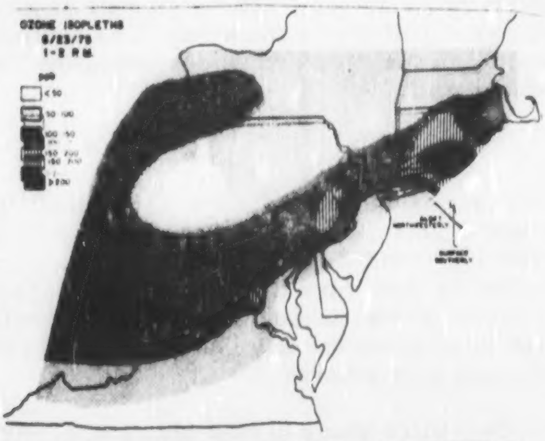
OZONE ISOPLETHS
6/23/75
1-2 P.M.
ppb
<50
50-100
100-150
150-200
>200
ALOFT NORTHWESTERLY
SURFACE SOUTHERLY

Figure 10-9. Ozone isopleths for the 1300-1400 time period of June 23, 1975, constructed using data from a network of ground-based sampling stations.

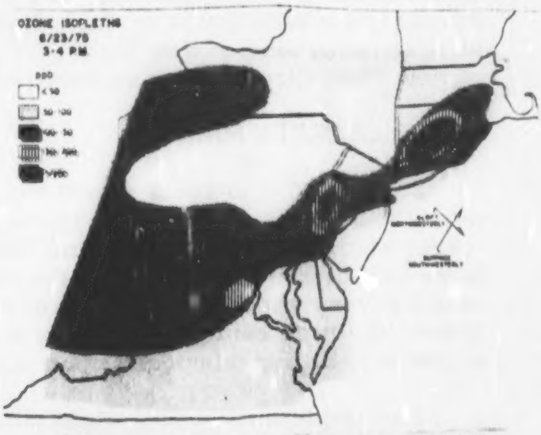
OZONE ISOPLETHS
6/23/75
3-4 PM
ppb
<50
50-100
100-150
150-200
>200
ALOFT NORTHWESTERLY
SURFACE SOUTHWESTERLY

Figure 10-10. Ozone isopleths for the 1500-1600 time period of June 23, 1975, constructed using data from a network of 95 ground-based sampling stations.

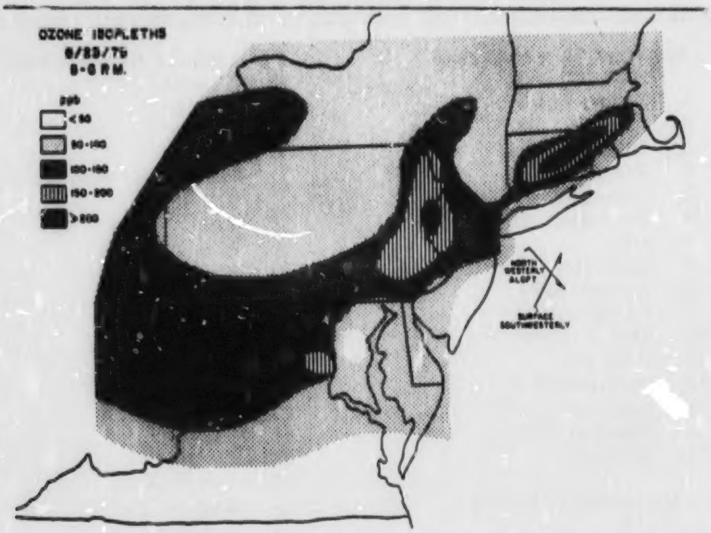
OZONE ISOPLETHS
6/23/75
5-6 P.M.
ppb
<80
80-100
100-150
150-200
>200
NORTH WESTERLY ALOFT
SURFACE SOUTHWESTERLY

Figure 10-11. Ozone isopleths for the 1700-1800 time period of June 23, 1975, constructed using data from a network of 95 ground-based sampling stations.

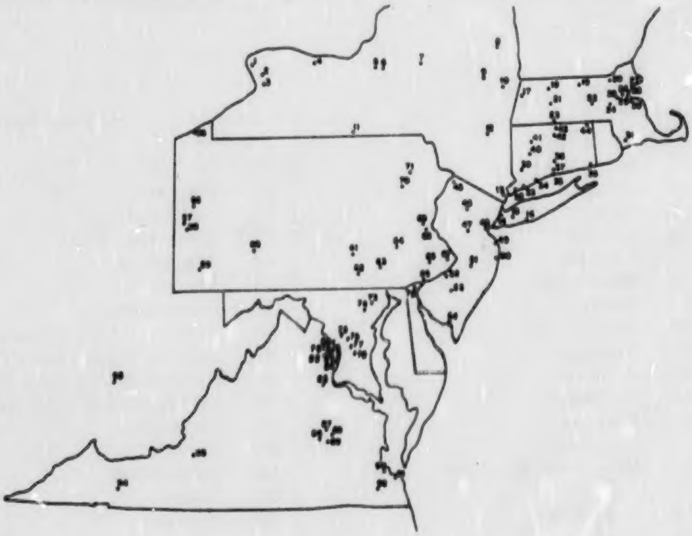

Figure 10-12. Geographic location of the 95 ground-based ozone sampling sites.

Table 10-1. LISTING OF MONITORS SUPPLYING DATA USED IN MAKING OZONE ISOPLETHS - BY STATE

New York State Monitors

1. Niagara Falls
2. Amherst
3. Buffalo No. 1
4. Rochester
5. Syracuse No. 1
6. Syracuse downtown
7. Utica
8. Glens Falls
9. Schenectady
10. Rensselaer
11. Elmira
12. Kingston
13. Mamaroneck
14. Roosevelt Island
15. Eisenhower Park
16. Babylon

Massachusetts Monitors

17. Pittsfield
18. Greenfield
19. Fitchburg
20. Lowell
21. Amherst
22. Worcester
23. Springfield
24. Framingham
25. Waltham
26. Medford
27. Salem
28. Cambridge
29. Boston
30. Quincy
31. Fall River

Connecticut Monitors

32. Greenwich
33. Stamford
34. Bridgeport
35. New Haven
36. Groton
37. Hamden
38. Middletown
39. Danbury
40. Morris Dam
41. Torrington
42. Windsor
43. Enfield
44. Eastford

New Jersey Monitors

45. High Point
46. Chester
47. Somerville
48. Bayonne
49. Sandy Hook
50. Asbury Park
51. McGuire Air Force Base
52. Camden
53. Ancora
54. Bivalve

Pennsylvania Monitors

55. Erie
56. New Castle
57. Beaver Falls
58. Baden
59. Charleroi
60. Johnstown
61. Harrisburg
62. York
63. Lancaster
64. Reading
65. Chester
66. Norristown
67. Bristol
68. Bethlehem
69. Allentown
70. Wilks-Barre
71. Scranton

Delaware Monitors

72. Wilmington

Maryland Monitors

73. Baltimore city, Calvert and 22nd
74. Baltimore city, Green and Lombard
75. Bethesda
76. Silver Spring
77. Cheverly
78. Suitland

Virginia Monitors

79. Fairfax
80. McLean
81. Seven Corners
82. Shirlington Road
83. Alexandria
84. Engleside
85. Fredericksburg
86. Richmond City, Spencer Road
87. Richmond City, State Fair Grounds
88. Richmond City, McGuire VA Hospital
89. Richmond City, 501 North 9th Street
90. Hampton
91. Norfolk
92. Nansemond
93. Salem
94. Marion

West Virginia Monitors

95. Charleston

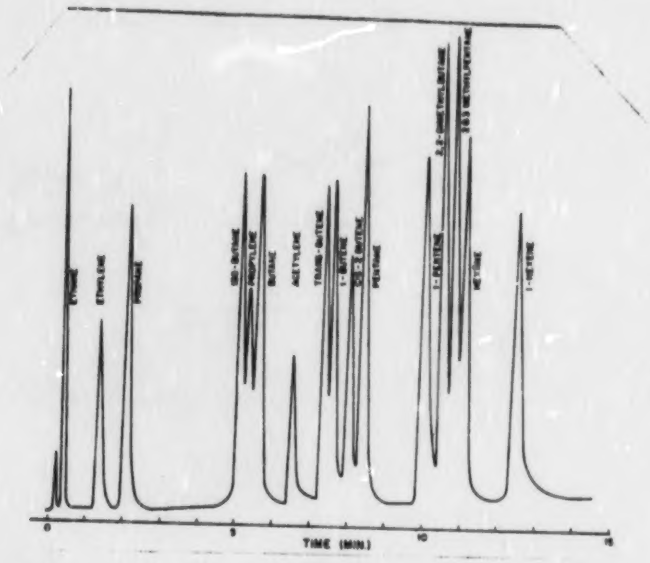

Figure 10-13. Composite calibration chromatogram.

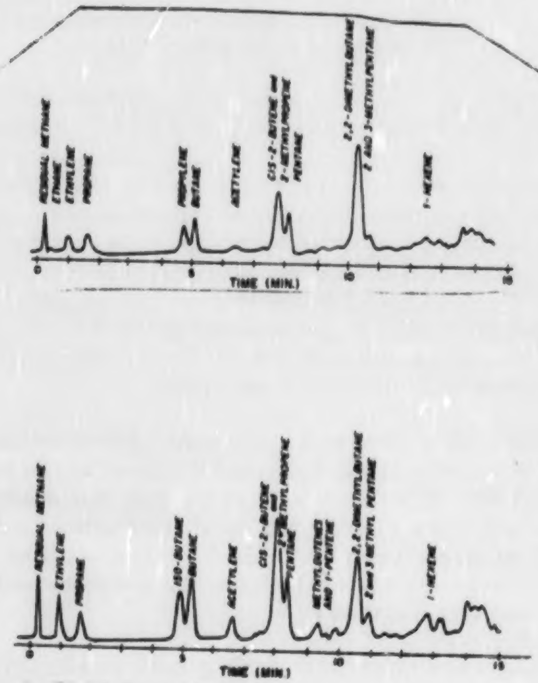

Figure 10-14. Some results of detailed hydrocarbon analyses for typical ambient air sample.

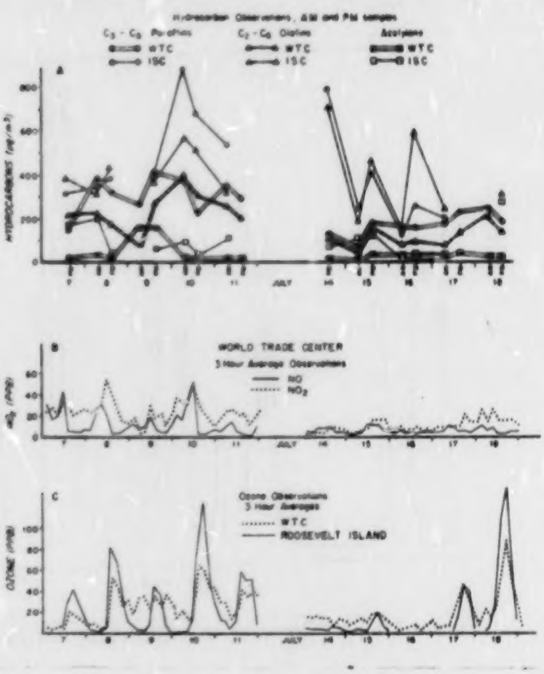

Figure 10-15. Hydrocarbon, nitrogen oxides, and ozone observations during study periods of July 7-11 and 14-18 in New York City.

record. Oxides of nitrogen and ozone were monitored continuously and plotted as 3-hour average values in Figures 10-15B and 10-15C, respectively.

Certain hydrocarbon resolutions in the area of the butenes and pentanes were difficult with the analytical procedure used and it is quite possible that our identification of cis-2-butene and 2-methylpropene includes a significant amount of isopentane. Mr. William Lonneman of EPA reports that one typically finds the isopentane-pentane pair upon chromatographic analyses of urban air. This would somewhat affect the olefin and paraffin values plotted in Figure 10-15A. Nonetheless, significant levels of hydrocarbons were found at the WTC to produce high ozone levels through photochemical reactions with oxides of nitrogen.

Our data indicate that a somewhat different hydrocarbon composition exists at the WTC and ISC locations, indicating different degrees of source influences or reactive losses during advection. There were days during the study period, however, when several compounds had very similar ratios at both sites, indicating simple dilution. Winds during the first week were variable from the southeast to northeast; during the second week, winds were consistantly from the south to southwest. There were heavy rains from July 14 through July 16.

High ozone levels were observed during both weeks, but very low ozone was observed during the period of heavy rain. During the first week, NO and NO_2 levels of 20 to 60 ppb were observed during the morning with approximately 400 to 800 $\mu g/m^3$ hydrocarbon levels at WTC. On July 17 and 18, both hydrocarbon and NO_x levels were reduced, yet significant ozone buildup occurred. Although there was a reduction of absolute values, a comparison of HC/NO_x ratios on the mornings of July 10 and 18 shows a higher ratio on the 18th. Although it must be cautioned that the air parcels observed in the morning and afternoon may have different chemical composition histories, which invalidates comparison of morning hydrocarbon-NO_x levels with afternoon O_3 levels, it is plausible that significant photochemical ozone production has been observed.

There is evidence that the WTC was above a low level inversion on the mornings of July 9 and 10, conditions similar to those observed on June 23 when the vertical O_3 profile in Figure 10-5 was made. On July 18 the morning sounding at Fort Totten, taken at 0700 hours, showed a 1.5°C inversion between 300 and 410 meters; therefore, the WTC was about level with the base of this early morning inversion. Thus, it is also possible that a high level (approximately 100 to 150 ppb) of ozone could exist in air layers aloft (2000 to 5000 feet) on these dates and that an upper air layer, upon mixing with lower levels following inversion dissipation, could contribute significantly to the afternoon O_3 peak.

It is likely that the processes of photochemical production of ozone, advection of ozone, mixing of ozone rich upper air with ozone depleted lower air below an inversion, and ozone scavenging by NO and surface reactions all play significant roles in generating the magnitude and patterns of ozone concentrations observed at ground level stations. The importance of each of these processes in any instance may well depend upon the site locations, pollutant inputs, and meteorological conditions at the time.

11. OZONE FIELD AUDITS FOR 1975 NORTHEAST OXIDANT TRANSPORT STUDY

Thomas M. Spittler
U.S. Environmental Protection Agency, Region I
Boston, MA

In order to assist the Air Branch in its evaluation of ozone data collected in New England during the 1975 ozone season, and in order to provide a common reference point for intercalibration of ozone sensors for all participants in the Northeast Oxidant Transport Study, the Technical Support Branch, Surveillance and Analysis Division, EPA Region I, undertook an extensive audit program covering the period May 20 to November 14, 1975. During this time period, 74 separate audits were performed on field ozone sensors.

Active participants in the Transport Study included the states of Connecticut, Massachusetts, Rhode Island, and New Hampshire; portable trailers were set up and operated by groups from the Research Triangle Park and Las Vegas Environmental Protection Agency Laboratories as well as by contractors from Battelle Institute, Columbus, OH, and Washington State University. The latter groups also provided planes equipped with ozone monitors for overflight data. Additional audits were made late in the season on ozone sites in Burlington, VT, and Portland, ME. Finally, interlaboratory calibrations were performed on August 14 with the Interstate Sanitation Commission and the State of Connecticut at Greenwich, CN, and on a National Bureau of Standards ozone generator shipped to the Region I laboratory in November. This calibrator was then loaned to the states of Massachusetts, Connecticut, and Rhode Island as well as to a private research laboratory before being returned to NBS for post calibration. Table 11-1 shows the various sites by name, collaborator, and geographic location.

AUDIT TECHNIQUE

Because of the need to recheck calibration of our ozone generator after each audit trip, field audits were all made as 1-day trips. Prior to a field audit, the ozone generator (AID Model 565) was calibrated in our laboratory using the neutral buffered potassium iodide (KI) technique (F.R. 36, No. 228, 22393-22395). During the period May 20 to June 18, 1975, only a few KI calibrations were performed. An in-house Bendix O_3 monitor was used to record these calibrations. Before and after field audits, the ozone generator was checked against this Bendix monitor. The KI technique was subsequently reevaluated at EPA-RTP, and several modifications were proposed in a draft memorandum dated April 14, 1975. The proposed modification to Section 5.10.1 substitutes a midget impinger for the "Mae West" bubbler pictured in the original published method. The accompanying statement is "MSPEB and others have found that midget impingers recover up to 15 percent more I_2 than the Mae West type bubbler." At the EPA Region I laboratory, the Mae West bubbler had been in use prior to this modification. Indeed it continues in use to this day. It has been our experience that the Mae West bubbler does indeed cause lower I_2 recovery (about 15 percent) when the sampling flow is reduced from 800 to 300 cm^3/min in the bubbler, but at a flow rate of 800 cm^3/min, we find no difference between the Mae West and midget impinger bubblers.

Table 11-1. LOCATION OF OZONE COLLABORATOR SITES

State sampling sites	State
Salem	Massachusetts
Wellington	
Quincy	
Framingham	
Worcester	
Amherst	
Eastford	Connecticut
Enfield	
Windsor	
Middleton	
Hamden	
New Haven	
Manchester	New Hampshire
Nashua	
Providence	Rhode Island
Scituate Reservoir	

Special sampling sites	Location
Battelle	Simsbury, CN
Washington State University	Groton, CN
EPA-RTP	Quincy, MA
EPA-LV	Weymouth, MA
State of Connecticut Laboratories	Greenwich, CN
EPA, Region I	Needham, MA

On or about June 18, 1975, an inadvertent change was made in the Region I laboratory procedure for calibrating ozone generators. A new team assumed responsibility for ozone calibration and arbitrarily chose a flow of 300 to 400 cm^3/min for collecting ozone in the Mae West bubblers. Previous calibrations (in 1974 and early 1975) were made using a flow of 800 cm^3/min. Both flows were well within the 200 to 1000 cm^3/min range recommended. Prior to this change, 16 field audits were performed using the high-flow calibration data. Subsequent to this change in flow, an active program of field audits was conducted based on the low-flow calibration.

On or about September 6, 1975, a summary of the summer audits was begun. At this time, a pronounced shift in audit data was noted. Values at all sites audited after June 18 were found to have shifted upward, and an explanation was sought. Detailed examination of laboratory record books finally pointed to the change in sampling flow from 800 to 300 cm^3/min as one possible cause. A careful investigation of this flow problem did indeed reveal that a consistent loss of about 15 percent was experienced when the lower flow was used. All field audits between June 19 and September 6 had been based on direct calibration of the ozone generator by the KI method. A tabulation of these data showed very consistent results (Table 11-2). Examination of recorder charts from an in-house Bendix ozone monitor used to verify all calibrator recordings before and after audits performed during the period April 20 to June 18 also showed good consistency (Table 11-3). The two sets of data are plotted in Figure 11-1. As may be readily seen, there is a consistent difference of about 16 percent between the two curves over the useful concentration range (0.1 to 0.3 ppm). This discrepancy agreed well with the 14 percent difference found during our study of the flow problem and the 15 percent difference discussed in the April 14 document from Research Triangle Park. Table 11-4 shows some of the data developed during this study. The large discrepancy at a sleeve setting of 200 indicates the problem inherent in attempting KI calibration of an O_3 generator at levels below 0.1 ppm O_3. It should be noted that the data in Table 11-4 were developed on a different generator (II) than the data used in Figure 11-1 (generator I). Ozone output versus sleeve setting is not directly comparable between generators owing to difference in lamp temperature, lamp output, etc.

Table 11-2. NEUTRAL BUFFERED KI CALIBRATION DATA, JUNE 20 TO SEPTEMBER 4, 1975, SAMPLE FLOW 300 TO 400 cm^3/min

Date	O_3, ppm, at sleeve setting 300	O_3, ppm, at sleeve setting 500	O_3, ppm, at sleeve setting 700
6/20	0.08	0.15	0.21
6/27	0.10	0.17	0.22
6/30	0.09	0.16	0.22
7/9	0.08	0.15	0.21
7/15	0.09	0.17	0.23
7/18	0.08	0.16	0.22
7/21	0.08	0.15	0.21
7/29	0.08	0.15	0.21
8/6	0.097	0.16	0.21
8/14	-	0.16	0.21
8/27	0.097	0.156	0.217
8/28	0.095	0.15	0.205
9/14	0.095	0.145	0.20
Average	0.088	0.156	0.213

Table 11-3. BENDIX INSTRUMENT RESPONSE TO TWO SETTINGS OF AID GENERATOR DURING PERIOD MAY 20 TO JUNE 17, 1975

(KI calibration at flow of 800 cm^3/min)

Date	800 sleeve setting	400 sleeve setting
5/20	0.30	0.13
5/21	0.30	0.145
5/27	0.295	0.15
5/28	0.295	0.155
6/4	0.29	-
6/10	0.30	0.15
6/13	0.295	0.15
	0.295	0.14
6/16	0.29	-
6/17	0.32	0.16
Average	0.297	0.148

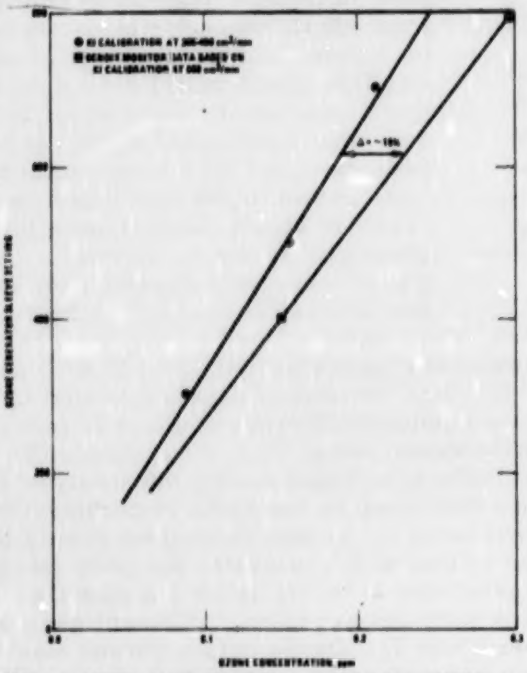

Figure 11-1. KI calibration curves for ozone at sample flow rates of 300-400 cm^3/min and 800 cm^3/min.

Table 11-4. COMPARISON OF KI CALIBRATION USING FLOWS OF 300 AND 800 cm^3/min

Date	Generator sleeve setting	Flow cm^3/min	Concentration, ppm	Percent difference
9/22/75	800	856 289	0.328 0.273	17
	600	856 289	0.246 0.215	13
9/24/75	800	861 294	0.330 0.284	14
	600	861 294	0.246 0.216	12
Average				14

Based on this study, all field audits made during the period June 19 to September 5 were recalculated using a corrected set of values of O_3 level versus sleeve settings. Corrections were taken from Figure 11-1 using the 800 cm^3/min flow data.

AUDIT RESULTS

Figures 11-2 to 11-4 are graphical representation of audit data by site. Audit dates are arranged chronologically on the horizontal axis for a given site. The vertical axis represents percent deviation of audited values from the Region I calibrator. The average value of the deviations is indicated by a dot and the range of deviation is indicated by the bar. A circle around the dot indicates audits made prior to June 19 and after September 5, 1975. The remaining values were all subjected to the corrections explained above. An audit normally consists of four or five concentrations between 0.08 and 0.3 ppm.

The following observations are offered on the data illustrated:

1. Within a given agency (e.g., Connecticut, Massachusetts, Rhode Island), there is a high degree of self consistency.

2. It must be remembered that all data are referenced to the Region I calibration system. This system is itself subject to variations, and hence some of the divergent data could be accounted for by fluctuations in the auditing ozone equipment.

3. Data in Figure 11-4 require special attention: In the case of New Hampshire sites, no ozone generator was available to the agency, hence calibration of a sensor was performed by transporting the KI calibration equipment into the field. This procedure, in our experience, is subject to many sources of error. In the case of the four groups collaborating in the Transport Study, all contractors precalibrated ozone generators, then transported them 600 to 2000 miles and operated them for 2 months without benefit of laboratory support. Under these conditions, the degree of agreement must be considered good.

4. In support of the data adjustments discussed above, it is important to note that data for Massachusetts and Connecticut include two audits in each set (circled) that bracket the altered data (6/18-9/5/75). The limited range of variations within a given data set indicates that the modified data indeed fit into each set.

5. Because different calibration teams are used at different sites (especially in the case of Massachusetts), it is not surprising that a certain amount of variation from site to site will occur. This could reflect calibration team experience as well as individual site instrument performance.

6. Averaging all audit values, a mean value (relative to Region I calibrator) is -7.8 percent. A summary of audit data by collaborating groups is given in Table 11-5.

An attempt was made to determine some of the reasons for variations between collaborating groups. In a telephone inquiry, the chemist or technician responsible for KI calibration was asked specific questions about various points of analytical technique and data reduction. The responses are summarized in Table 11-6. As discussed

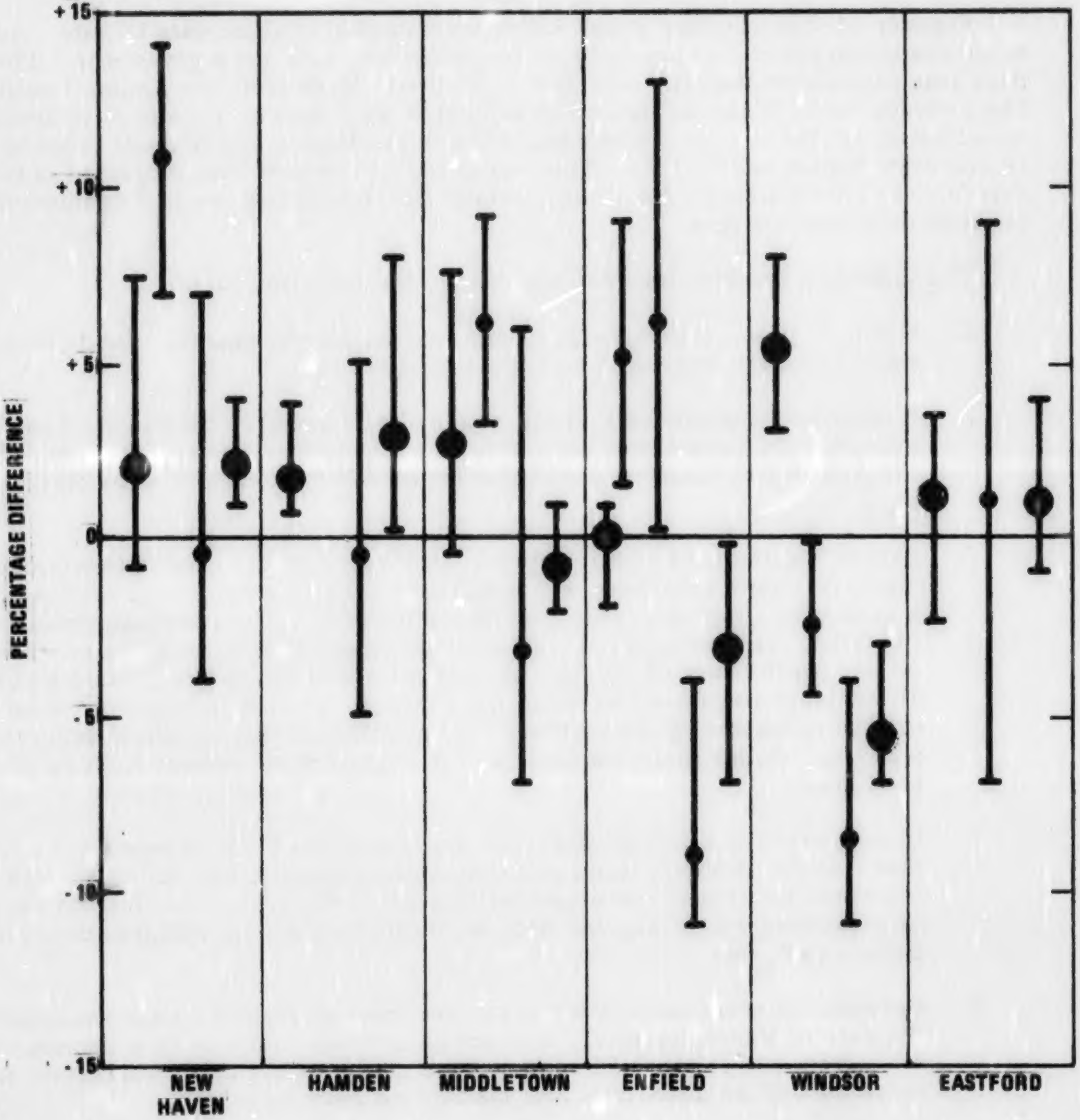

Figure 11-2. Ozone audit results at the Connecticut sampling sites.

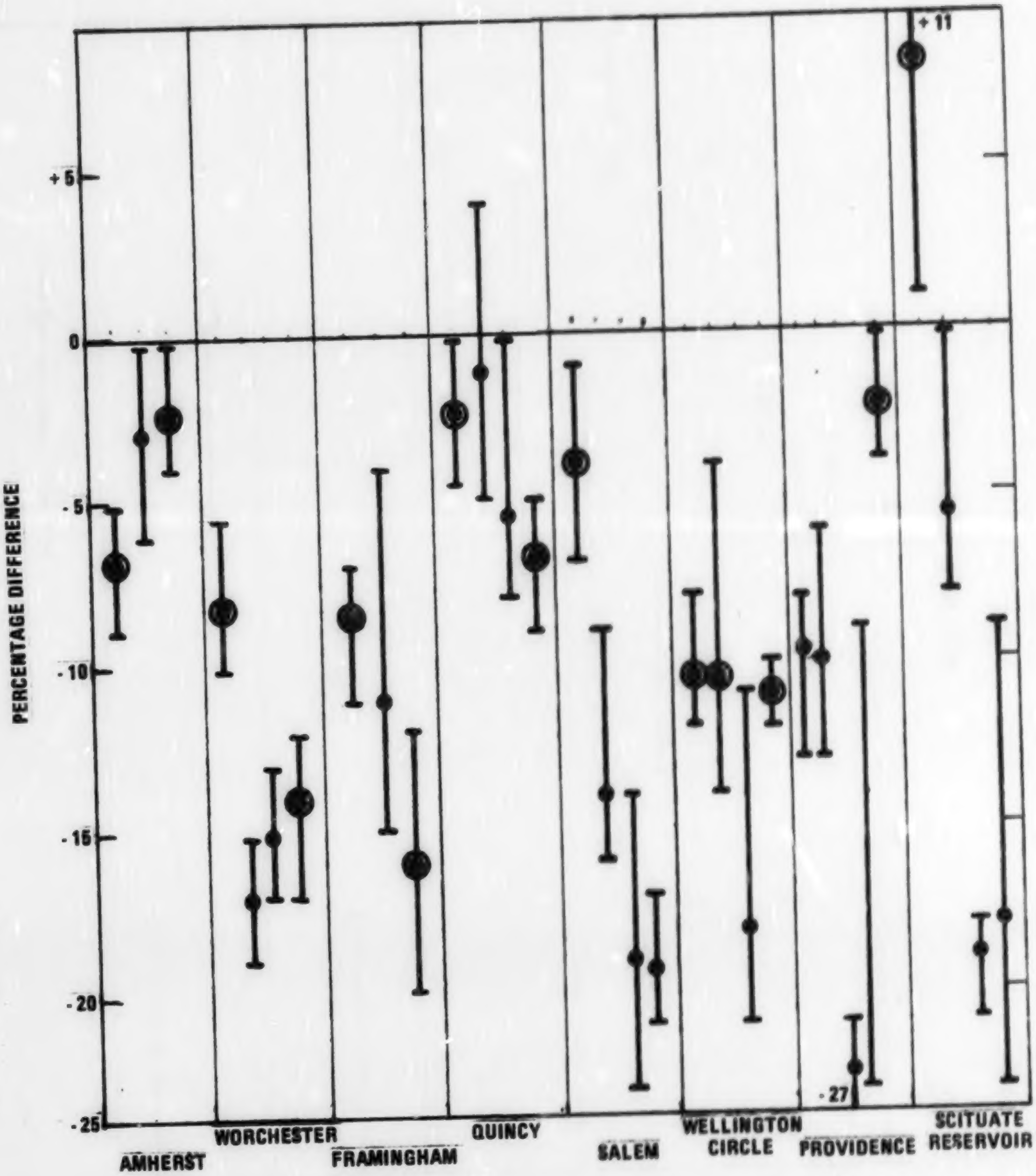

Figure 11-3. Ozone audit results for Massachusetts and Rhode Island sampling sites.

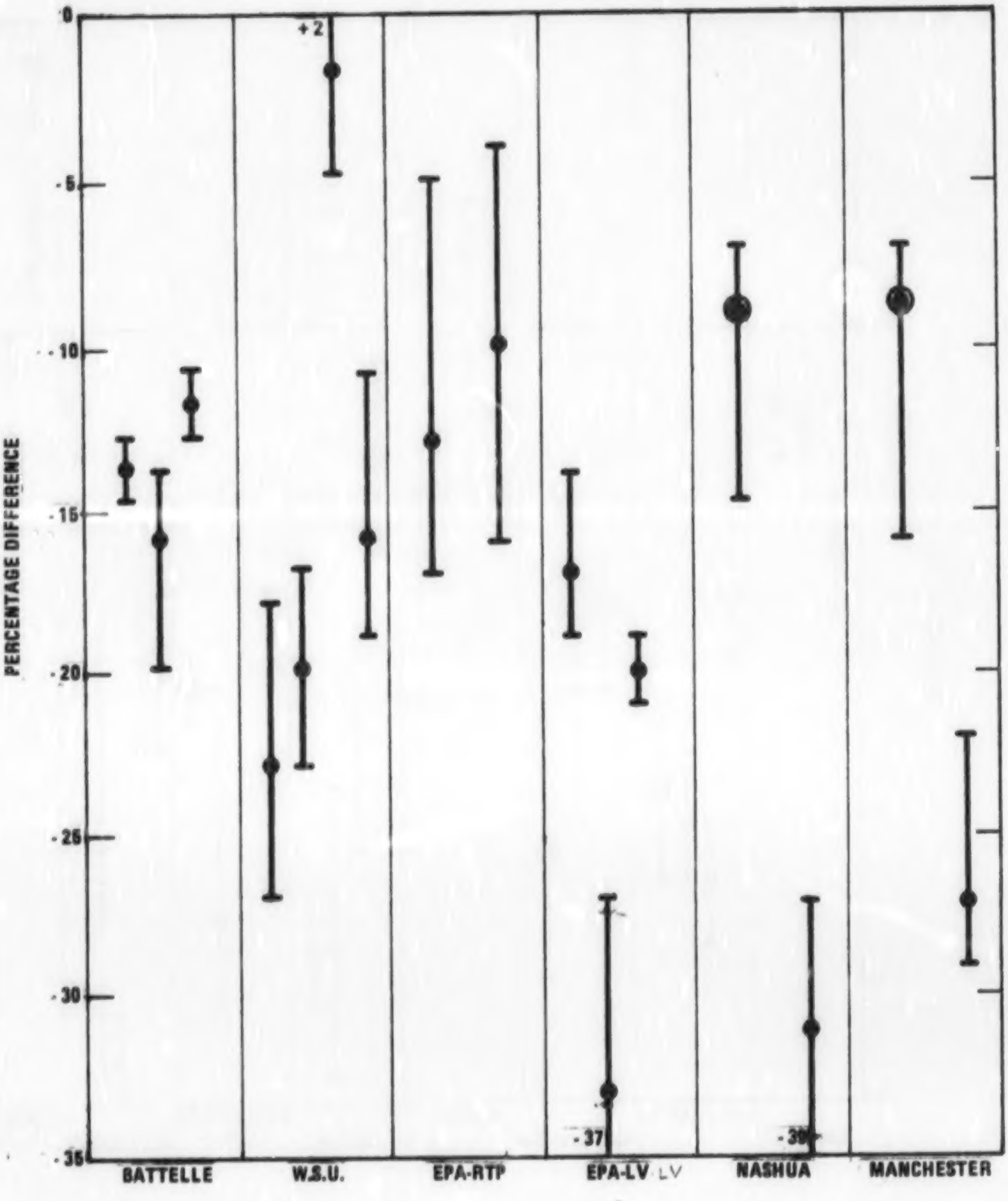

Figure 11-4. Ozone audit results for special study participants and for New Hampshire sampling sites.

Table 11-5. SUMMARY OF AUDIT DATA BY GROUP

Group or agency	Sum of percent diff.	Number of audits	Avg. percent diff.
Connecticut	+ 21.1	24	+ 0.88
Massachusetts	- 233	24	- 9.7
Rhode Island	- 93.4	9	- 10.4
New Hampshire	- 75.8	4	- 18.9
Contractors	- 200.5	13	- 15.4
Average			- 7.8

Table 11-6. VARIABLE PARAMETERS USED IN THE KI CALIBRATION METHOD

Collaborator	UV cell used, mm	Collec. device[a]	Collec. flow rate, l/min	Concen. range of calibra., ppm	Collec. time, min	Was I_2 curve calcu. by least sq	Chemist replying
EPA Region I	10	MWB	0.8	0.1 -0.3	10	Yes	E. Goffi
Same 6/18-9/5/75	10	MWB	0.3-0.4	0.1 -0.3	10	Yes	E. Goffi
Mass.	19	MI	0.8	0.1 -0.3	10	No	J. Clements
CN	10	MI	0.8	0.04-0.12	10	No	D. Gregorsky
RI	10	MI	0.5	0.1 -0.35	10	Yes	J. Cucco
NH	10[b]	MI	1.0	N.A.	10	No	A. Festa
EPA-RTP	10	MI	1.0	0.02-0.1	10-30	No	R. Seila
EPA-LV[c]							C. Bennett
Battelle	10	MI	1.0	0.1 -0.5	15	Yes	C. Spicer
WSU	10	MI	0.5	0.1 -1.0	15-30	No	E. Grimsrud
NBS	10	MI	1.0	0.1 -0.5	10	Yes	A. Hughes

[a] MWB--May West bubbler; MI--midget impinger.

[b] Circular curvettes.

[c] Calibration performed with long path UV photometer.

above, the variation in flow rate in the Mae West bubbler used by Region I caused a 14 percent difference in results. This point was checked by two groups (Massachusetts and Rhode Island) using their own midget impingers. Little or no variation in collection efficiency with flow rate was experienced in the impingers. This tends to verify the recommendation made by Research Triangle Park in their April 14, 1975 memo.

Where a low concentration range is used for calibration, several problems can occur: Low values for absorbance increase the chances of error. Small variations in the I_2 calibration curve can cause sizeable error, especially when the slope is only estimated and no intercept is taken into account. Where collection time exceeds 10 minutes, there is a well documented risk of losing some collection efficiency through decay of the absorbing species with time.

In such a complex procedure, other parameters will also effect results, e.g., type of ultraviolet instrument used, chemicals employed for standards and titration, impurities in the absorbing solution, etc. The present study points out a need to further specify operational steps within a collaborating group. Such an effort is being proposed for the Region I collaborators prior to the 1976 ozone season.

INTERLABORATORY CALIBRATIONS

Two interlaboratory calibrations were performed comparing ozone generators traceable to the National Bureau of Standards. On August 14, 1975, the Region I laboratory equipment was taken to Greenwich, CN, to be compared with a calibrator used by the Interstate Sanitation Commission (recently calibrated at NBS laboratories) as well as one used by the state of Connecticut. Data on this calibration are shown in Table 11-7. No attempt was made to precalibrate an on-site monitor used in this comparison. Each group simply fed four or five levels of ozone to the same monitor and recorded the values obtained. As may be seen, the agreement between the three calibrators was excellent.

Table 11-7. INTERLABORATORY CALIBRATION, GREENWICH, CN, AUGUST 14, 1975

Collaborator	Sleeve setting	Ozone generator, ppm	Ozone monitor response	Percent diff.	Average percent diff.
Interstate Sanitation Commission		0.077	0.071	- 7.8	
		0.080	0.074	- 7.5	
		0.108	0.10	- 7.4	
		0.214	0.208	- 2.8	- 6
Connecticut		0.107	0.094	-12	
		0.089	0.080	-10	
		0.063	0.059	- 6	
		0.056	0.048	-14	-10
EPA Region I	900	0.335	0.288	-14	
	700	0.260	0.225	-13	
	500	0.185	0.162	-12.4	
	300	0.11	0.098	-11	
	150	0.055	0.052	- 5.4	- 8.2

A second interlaboratory calibration was performed on an NBS calibrator. On November 12, 1975, a calibrator was received at the Region I laboratory from NBS. It was tested for 2 days using our KI method. Results were then compared to a calibration curve sent under separate cover from NBS. Subsequently, the calibrator was loaned to the states of Massachusetts, Connecticut, and Rhode Island and to a private laboratory (Environmental Research Technology) to enable these groups to check their KI techniques. Results of the tests are shown in Table 11-8. Data are calculated on percent difference $\frac{(NBS-X)}{NBS} \times 100$. Each group worked without the NBS calibration curve. Actual values were supplied at the termination of each study. Again, attention is drawn to the problem encountered with low levels of ozone. Only the ERT data show good results at low O_3 levels. This is so because an ozone monitor was used in their test. Good linearity at both high and low levels is to be expected in such a test. The generator supplied by NBS was not temperature controlled. Calibration was performed at 25°C. Each collaboratory was asked to note room temperature during their calibration runs. These temperatures are noted in Table 11-8. Each group noted a variation of about ± 1°C during their period of operation.

These interlaboratory calibrations indicate a high level of competence in the participating laboratories. When the additional steps involved in field calibration are taken into account, wider fluctuations must be expected. Here the range of variables includes different calibration equipment, competence of field personnel, field instrument stability, site suitability, and individual collaborator equipment performance as well as variations in the audit team performance and equipment. It is this set of variables which probably accounts for much of the variation found in Figure 11-1 data.

Table 11-8. INTERLABORATORY CALIBRATION, NATIONAL BUREAU OF STANDARDS CALIBRATOR

Generator No. 19 sleeve setting	NBS, ppm (25°C)	EPA, ppm (24°C)	Percent diff.	MA, ppm (26°C)	Percent diff.	RI, ppm (27°C)	Percent diff.	CN, ppm (17.5°C)	Percent diff.	ERT[a] ppm (21°C)	Percent diff.	Avg., ppm	Relative[b] standard deviation, percent
100	0.580[c]			0.541	-6.7								
90	0.495	0.476	- 3.9							0.462	-6.6		
80	0.420	0.410	- 2.3	0.415	-1.2	0.443	± 5.5	0.422	+0.5	0.408	-2.8	0.420	3.3
70	0.360	0.363	+ 1.0							0.343	-4.7		
60	0.300	0.294	- 2.0	0.290	-3.3	0.330	+10	0.297	- 1.0	0.298	-0.40	0.300	5.6
50	0.242									0.238	-1.6		
40	0.192	0.194	+ 1.0	0.184	-4.2	0.207	+10	0.187	- 2.6	0.187	-2.6	0.192	4.7
30	0.141									0.138	-2.1		
20	0.092	0.089	- 3.3	0.084	-8.7	0.096	+ 4.3	0.094	+2.6	0.091	-1.0	0.091	5.5
10	0.042	0.035	- 16.7[d]							0.041	-2.4		
Avg.			- 1.6		-4.8		+ 7.5		-0.13		-3.1		

[a] Data generated by running NBS calibrator vs. precalibrated McMillan O_3 Sensor.

[b] Calculated by method of Dean and Dixon.

[c] Extrapolated value.

[d] Discarded as outlier by the Q test of Dean and Dixon.

12. SIMULATION OF OXIDANT AND PRECURSOR TRANSPORT IN A SMOG CHAMBER

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Figure 12-1 is a diagram of the Research Triangle Institute's smog chamber installation. The system is composed of four outdoor chambers (each 27 cubic meters in volume) made of 5-mil FEP Teflon on aluminum frames. Each chamber has its own air cleaning system to oxidize hydrocarbons and remove oxides of nitrogen (NO_x).

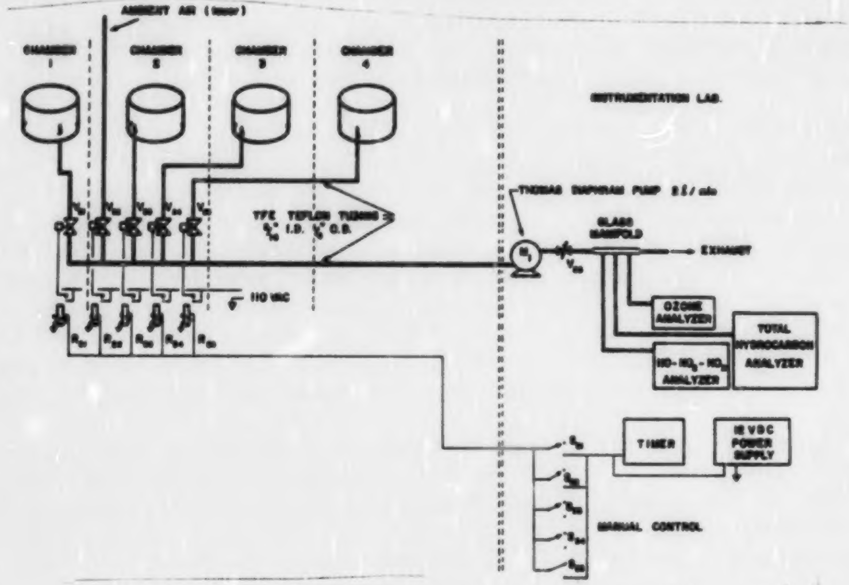
AMBIENT AIR
CHAMBER 1
CHAMBER 2
CHAMBER 3
CHAMBER 4
INSTRUMENTATION LAB.
THOMAS DIAPHRAGM PUMP
TFE TEFLON TUBING
I.D.
O.D.
GLASS MANIFOLD
EXHAUST
110 VAC
OZONE ANALYZER
TOTAL HYDROCARBON ANALYZER
ANALYZER
TIMER
VDC POWER SUPPLY
MANUAL CONTROL

Figure 12-1. Diagram of RTI Outdoor Smog Chamber.

The study reported here in brief was initiated, under Environmental Protection Agency sponsorship, to study the behavior of O_3 concentration under simulated conditions of transport of oxidant and its precursors downwind from urban environs. To simulate movement from the cities, chemical pollutant systems were irradiated for multiple daylight periods and subjected to a period of dilution with clean air. Data for three dilution rates are reported: 0.0 percent dilution (i.e., batch), 77.5 percent dilution, and 95 percent dilution in 24 hours. After dilution, the chambers were run in a batch mode with no additional dilution.

Initial reactant charges were 1 to 10 parts per million carbon (ppmC) of a surrogate urban mixture and 0.1 to 1.0 part per million (ppm) of NO_x, of which 20 percent was nitrogen dioxide (NO_2). The nonmethane hydrocarbon (NMHC) to NO_x ratios were chosen to be from 7 to 20.

The results of the study have been summarized, in part, in a series of tables similar to Table 12-1. The first four columns after the data and chamber number provide information about the first day's behavior of the system. This series of runs was diluted 95 percent for 24 hours starting at the time of NO_x crossover (at about 0830). In chamber 1, the NMHC charge was about 7 ppmC and the NO_x was about 1.0 ppm with a ratio of 7. Maximum ozone (O_3) concentration in chamber 1 was about 1.1 ppm the first day. The next column indicates whether the following data are from the second or third day of irradiation. The NO_x concentrations at sunrise were in the part per billion (ppb) range. The NMHC/NO_x ratios were high; for the whole set of experiments, they ranged from 27 to over 300. On the second and third days, gas chromatographic analysis of the remaining hydrocarbons showed a preponderance of alkanes and aromatic compounds, with alkenes virtually exhausted except for a few tens of parts per billion of ethylene that usually remained.

The maximum O_3 concentrations obtained in the second and third days were, in most cases (in all cases in Table 12-1), above the National Ambient Air Quality Standard (NAAQS) for photochemical oxidant. The net O_3 concentrations generated (i.e., the difference between the morning minima and the afternoon maxima) were also almost all greater than the NAAQS despite extremely low NO_x concentrations.

Table 12-2 represents another type of summary and analysis of the O_3 generative data from the second and third days of irradiation. In Table 12-2, both the NO_x data and the NMHC/NO_x ratios have been stratified by numerical range and the net O_3 concentrations associated with a particular combination have been listed in the appropriate squares. Averages of individual boxes, vertical columns, and horizontal rows, are indicated. Although not illustrated, the same treatment was afforded the maximum O_3 concentrations and then both the net O_3 and the maximum O_3 concentrations were compared for various combinations of NMHC concentration range and NMHC/NO_x ratios. Ranges of NO_x and NMHC concentration were arbitrarily selected to provide a spread of ratios. These indicated comparisons are plotted in Figures 12-2 to 12-4.

In Figure 12-2, it can be seen that maximum, minimum, and net O_3 concentration increased with increasing NO_x. As the maximum O_3 concentration increased, so did the minimum. The divergence between maximum and net O_3 concentrations as the NO_x concentration increased was due to O_3 left over from the day before. A similar phenomenon with increasing NMHC concentrations can be seen in Figure 12-3.

In Figure 12-4, O_3 concentration was plotted against NMHC/NO_x ratios. Here there was a maximization of O_3 concentration (both maximum and net) in the 55 to 99 ratio range.

A so-called "dilution effect" on O_3 generation was mentioned in an earlier presentation. It has previously been noted by others that a reduction in initial concentrations of reactants (at the same ratio) did not produce a proportional reduction in the subsequent O_3 maximum. Similar phenomena have been observed under dynamic dilution in this study. An example employing second day data is illustrated in Figure 12-5. Similar initial concentrations and conditions of solar irradiation existed in the three cases. As can be seen, a 95 percent dilution of the system in 24 hours (ending about 0830 on the second day) produced only a 40 percent reduction in maximum O_3. The net O_3 generated in the 95 percent dilution (0.26 ppm) was actually greater than the net generated in the batch system (0.20 ppm). The efficiency of O_3 generation (per NO_x molecule) is increased by dilution. This so-called dilution effect is one of the processes helping to deliver high O_3 concentrations to nonurban areas.

Table 12-1. SELECTED RESULTS FROM THE JULY 28-30 THREE-DAY CHAMBER RUNS

Chamber No. Date	Percent dilution, time of dilution initiation	Initial NMHC/NO_x concentrations, ppmC/ppm	NMHC/NO_x Ratios	Maximum O_3 first day, ppm	Subsequent days	Precursors (ppm) at sunrise		NMHC/NO_x Ratios	Min. O_3, ppm	Max. O_3, ppm	Net O_3, ppm	Σ Solar rad. at O_3 max. (Langley's)
						NO_x	NMHC					
Chamber No. 1	95% @ 0830	7.35 0.989	7.432	1.062	2	0.007	0.84	120.000	0.023	0.286	0.263	515.40
July 28-30					3	0.009	0.85	94.444	0.050	0.240	0.190	421.20
Chamber No. 2	0840	4.33 0.235	18.426	0.604	2	0.003	0.77	256.667	0.006	0.212	0.206	535.20
July 28-30					3	0.005	0.76	152.000	0.035	0.190	0.152	420.60
Chamber No. 3	0840	4.67 0.731	6.389	0.667	2	0.005	0.48	96.000	0.013	0.214	0.201	534.60
July 28-30					3	0.005	0.55	110.000	0.037	0.190	0.153	397.80
Chamber No. 4	0850	1.17 0.107	10.935	0.325	2	0.002	0.55	275.000	0.003	0.175	0.172	541.20
July 28-30					3	0.003	0.63	210.000	0.042	0.167	0.125	427.20

Table 12-2. NET OZONE GENERATED ON SECOND AND THIRD DAYS OF IRRADIATION AS A FUNCTION OF OXIDES OF NITROGEN AND NONMETHANE HYDROCARBON/OXIDES OF NITROGEN RATIO

Range $\frac{\text{NMHC (ppmC)}}{\text{NO}_x\text{ (ppm)}}$	NO_x range, ppb			
	1 - 5	6 - 8	9 - 14	15 - 53
0-49			0.195 0.182^a 0.115 Avg. 0.164	0.181 0.154 Avg. 0.168
50-99	0.201 Avg. 0.201	0.124* 0.131* Avg. 0.128	0.312 0.190* 0.256 0.119* 0.230 0.177* 0.214 Avg. 0.214	0.365 0.344* 0.300 0.197 0.371 Avg. 0.315
100-199	0.152^a 0.123^a 0.217^a 0.054^a 0.153^a Avg. 0.140	0.263 0.257^a 0.250^a 0.068^a 0.150^a Avg. 189	0.123 0.033 0.094 0.285^a Avg. 0.134	0.150 0.238^a 0.135 0.228^a Avg. 0.188
200	0.076 0.173 0.206 0.129 0.172 0.125^a Avg. 0.147			
Average ozone	0.149	0.171	0.180	0.241

[a] Indicates third day values.

A term "fossil" O_3 has been coined (and should now be abandoned) to denote O_3 which is generated in urban environs and then drifts for some distance downwind. Prodigious distances of translation for undiminished O_3 levels are implied.

In order to see what light the smog chamber data shed on this phenomenon (i.e., the possible duration of O_3 in a spent and non-O_3-generating system), the nighttime half-lives of O_3 were calculated in chambers at a time when they were not undergoing mechanical dilution. Results are shown in Table 12-3. Maximum O_3 levels of the previous day are shown, and half-lives were calculated using the 0200 and 0500 concentrations. The table shows the 0200 concentrations and the calculated half-lives.

Half-life was calculated by removing the dark-phase clean chamber O_3 destruction rate constant (k_s). Assuming first order decay, half-life may be calculated as follows:

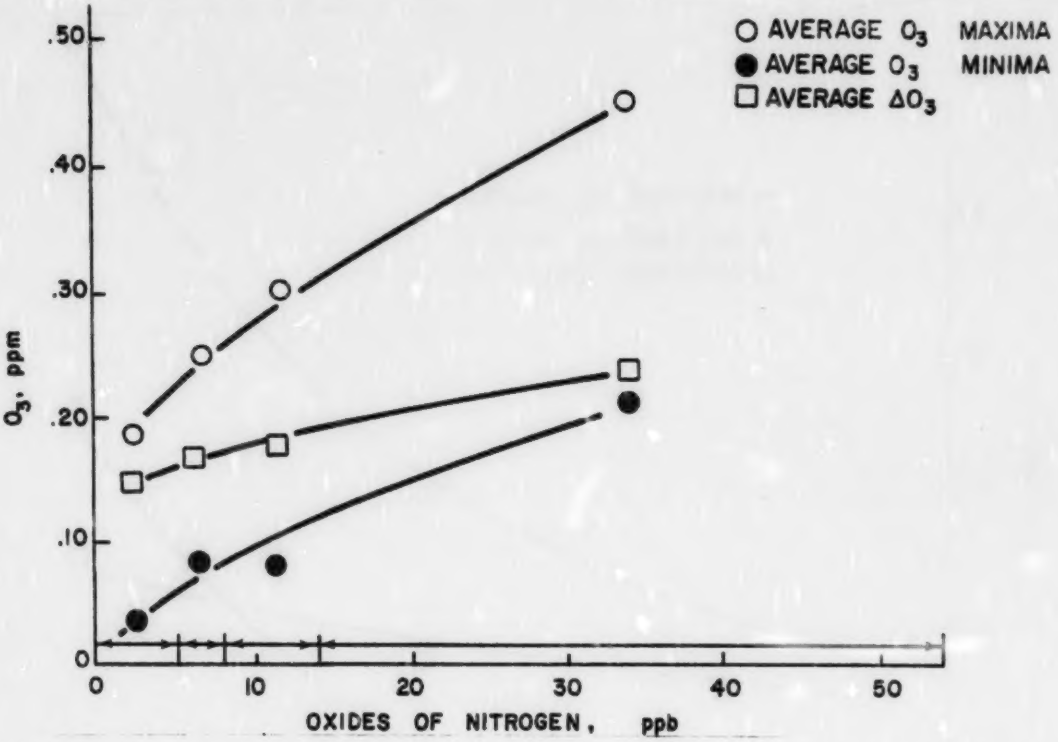

Figure 12-2. Average maxima, minima, and ΔO_3 concentrations as function of NO_x concentrations at sunrise on second and third days of irradiation.

$k_t t$ = $\ln \frac{c_{0200}}{c_{0500}}$

t = 3 hours

k_t = $(k_s + k_g)$

k_t = rate constant for O_3 destruction due to reaction with the chamber plus reaction with pollutant contents of the chamber (calculated)

k_s = rate constant for O_3 destruction by the chamber determined from O_3 - clean air mixtures in the dark

k_g = gas phase destruction of O_3 by contents of the experimental pollutant system

k_g = $k_t - k_s$

$t_{\frac{1}{2}}$ = $\frac{\ln 2}{k_g}$

Of the 24 values listed, 17 are below 20 hours, 5 others are below 60 hours, and 2 are rather large, 265 and 450 hours. The only field data the author has from which to

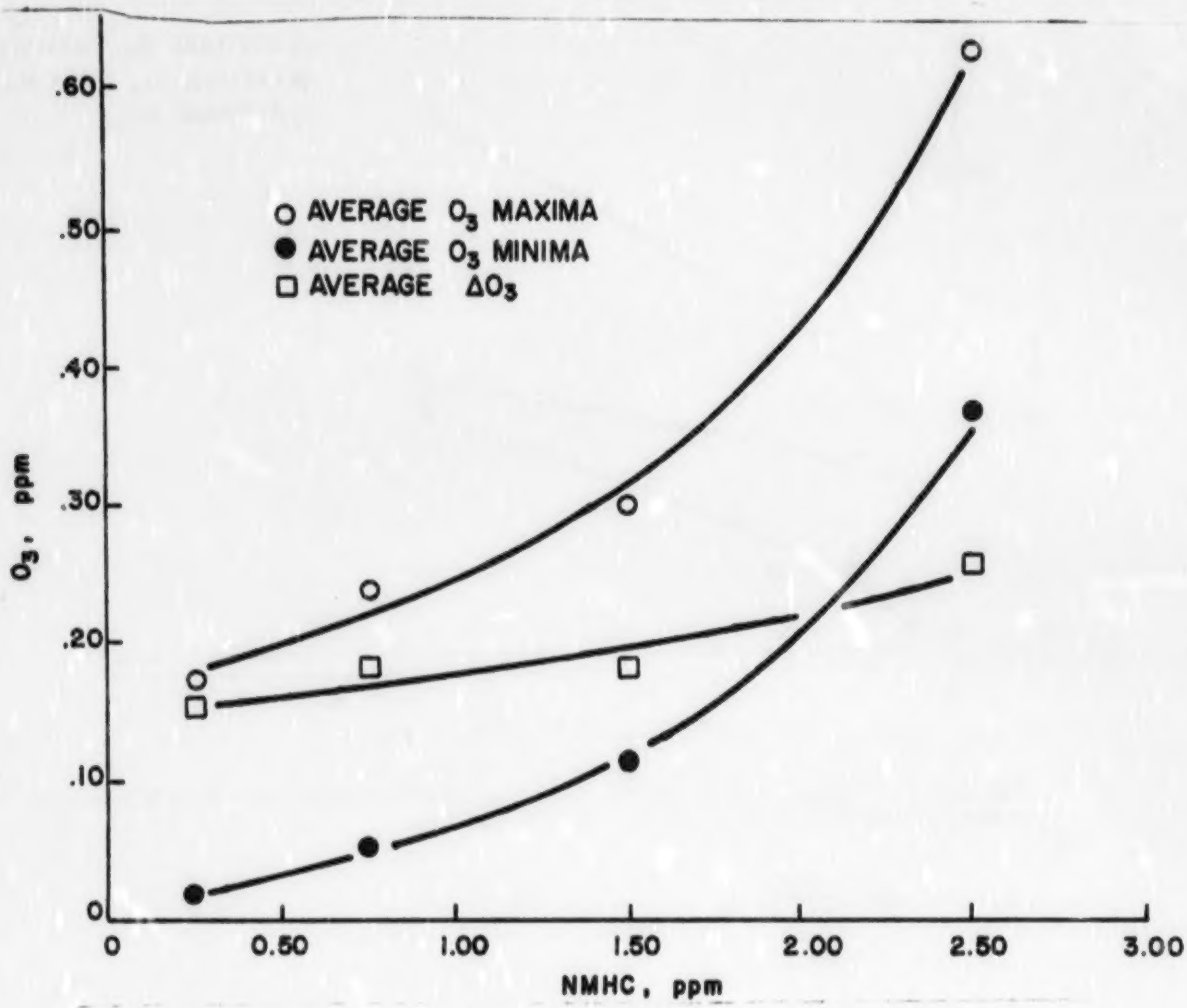

Figure 12-3. Average maxima, minima, and ΔO_3 concentrations as function of nonmethane hydrocarbon concentrations on second and third days of irradiation.

make an estimate of the dark phase half-life are shown in Figure 12-6. A series of vertical O_3 concentration profiles were taken with an aircraft on August 1, 1974, at Wilmington, OH. To obtain a rough estimate of what the O_3 half-life might have been, it was assumed that the profile at 0700 on August 2 was the same as that at 0700 on August 1. Assuming a first order decay from 1700 August 1 to 0700 August 2, the calculated O_3 half-life was 29.5 hours.

With half-lives of 20 to 30 hours, the amount of O_3 left over on the following morning can provide a high minimum on which to build a high maximum for the day. With half-lives of 20 to 30 hours, however, a parcel of so-called "fossil" O_3 cannot maintain high concentrations for more than a day or two without augmenting synthesis.

Chamber data of the second and third day are remarkably similar to field data. A major difference in the two kinds of systems was that after the initial charge no

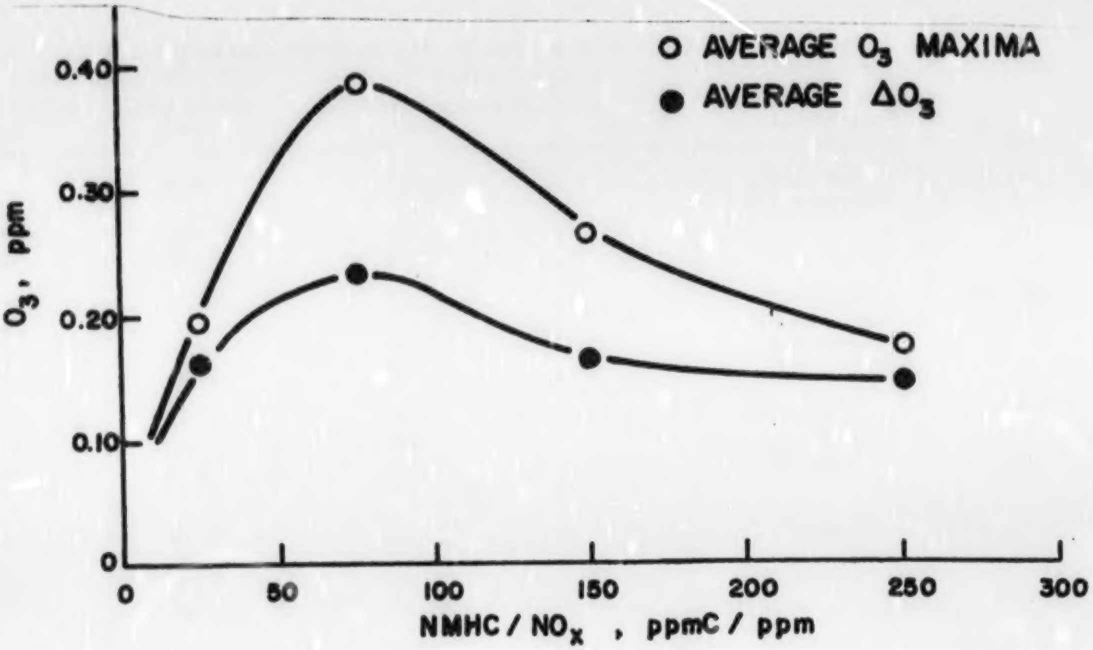

Figure 12-4. Average maxima and ΔO_3 as function of nonmethane hydrocarbon to oxides of nitrogen ratio.

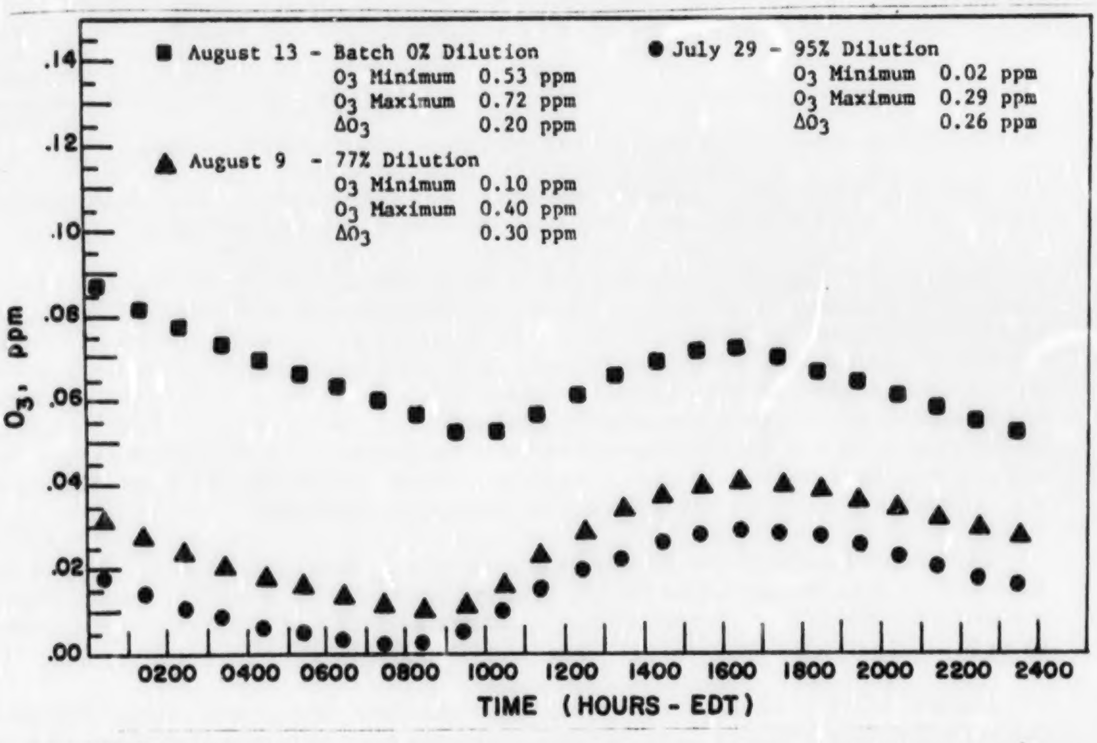

Figure 12-5. Ozone profiles over second day irradiations for same initial conditions and different dilutions in chamber 1.

Table 12-3. DARK-PHASE OZONE HALF-LIVES IN SMOG CHAMBER RUNS

Date	Experimental type	Chamber number	Max. [O_3] previous day, ppm	[O_3] at 0200, ppm	Half-life ($t_{1/2}$), hr
July 24	Dilution 95% [a] Initiated at 1700	1	0.185	0.066	4.3
		2	0.138	0.048	3.6
		3	0.119	0.038	11.6
		4	0.089	0.025	13.3
July 30	Dilution 95% Initiated at NO_x crossover	1	0.286	0.102	6.4
		2	0.212	0.085	6.2
		3	0.214	0.076	7.4
		4	0.175	0.083	7.8
August 6	Dilution 77% Initiated at NO_x crossover	1	0.479	0.311	14.9
		2	0.366	0.243	11.6
		3	0.350	0.213	10.0
		4	0.214	0.109	7.1
August 10	Dilution 77% Initiated at NO_x crossover	1	0.400	0.218	16.6
		2	0.293	0.175	14.2
		3	0.288	0.150	19.2
		4	0.179	0.109	14.2
August 13	Batch	1	1.378	0.776	33.5
		2	0.886	0.561	42.9
		3	0.997	0.567	50.3
		4	0.649	0.415	265.4
August 14	Batch	1	0.724	0.422	19.9
		2	0.525	0.333	27.2
		3	0.786	0.352	54.5
		4	0.336	0.252	449.6

[a] Mechanical dilution had been terminated prior to the time periods chosen for half-life calculations.

additional reactants were added to the chamber. To compare actual field conditions with second and third day smog chamber data, observe Figures 12-7 to 12-12.

Figure 12-7 depicts diurnal curves drawn from hourly O_3 averages at three Ohio stations in the summer of 1974. Note that the maxima are between 0.07 and 0.08 ppm, indicating that many of the individual concentrations making up the hourly averages were over the NAAQS. The time of maxima at the rural station was shifted more toward sundown than in city diurnal curves. Also the slope of the O_3 destructive side of the curve is less steep than the O_3 synthesis side of the curve. This is not generally the case in urban diurnal curves and can be attributed to the fact that in a relatively spent photochemical system out of touch with fresh pollutants (as auto exhaust in evening rushhour traffic) the O_3 destructive agents are depleted.

Figure 12-8 depicts the hourly averages of NO_x from the field obtained at the same time and in the same areas as the O_3 data in Figure 12-7. The NO_x concentrations ranged from about 2 to 12 ppb. Smog chamber second and third day values were 1 to 53 ppb. Calculated from average data, the NMHC/NO_x ratios were 27 to over 300.

Figures 12-9 to 12-12 compare field and chamber data graphically. Figure 12-9 contains the data from the first day of a smog chamber run in which there was no dilution. The data of the second and third days (Figures 12-10 and 12-11) both achieved maximum O_3 concentrations and net O_3 generation well over the NAAQS.

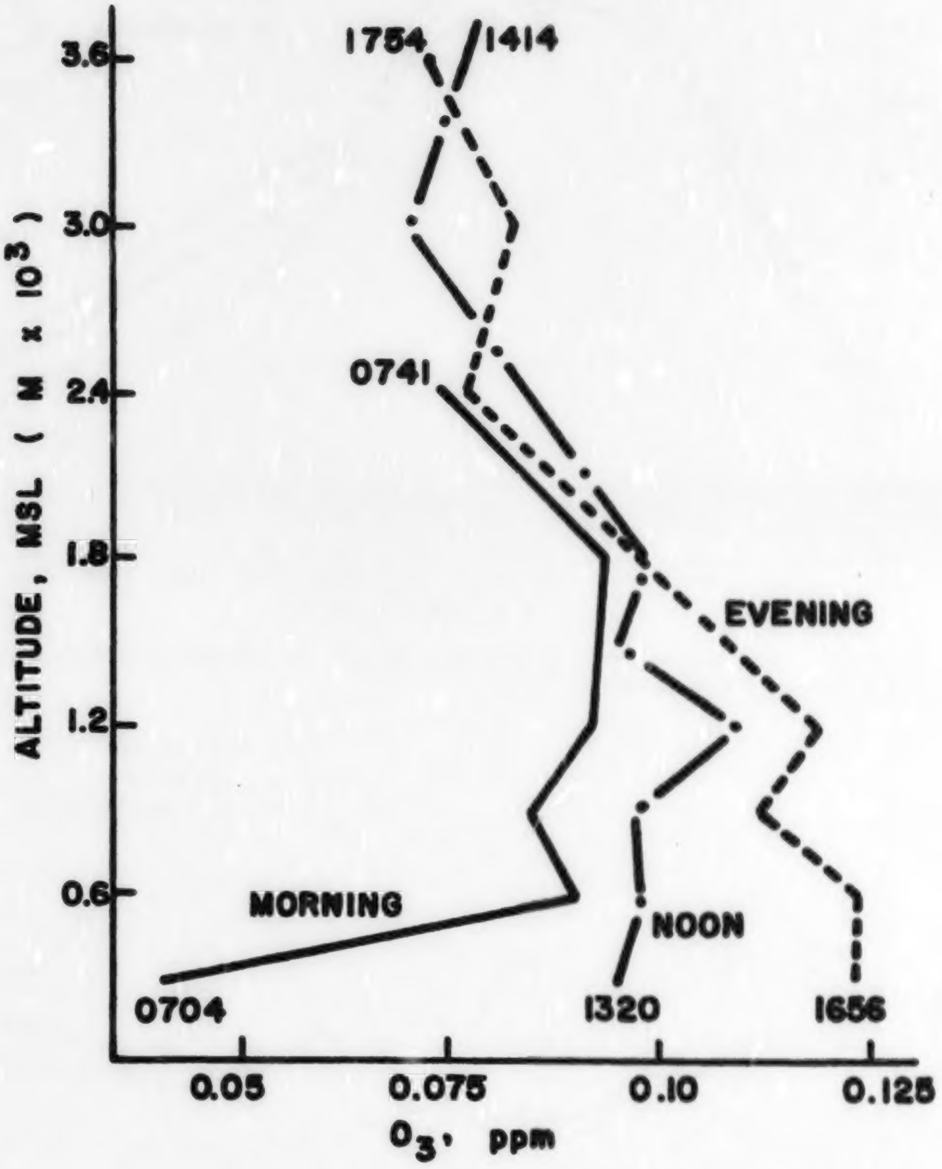

Figure 12-6. Vertical ozone soundings at Wilmington, Ohio, on August 1, 1974.

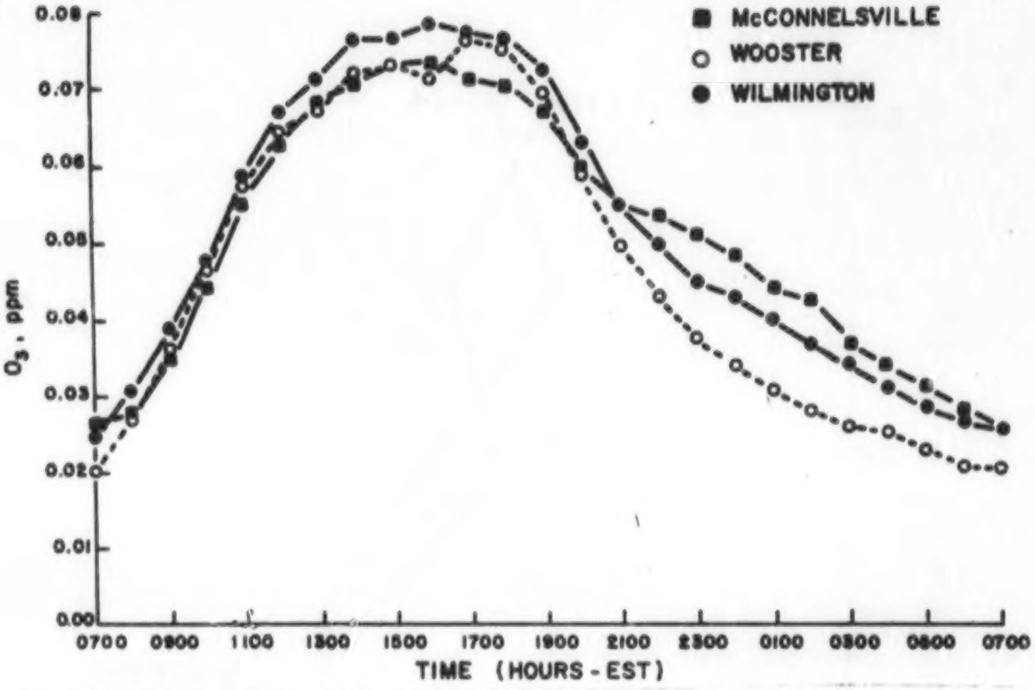

Figure 12-7. Mean diurnal O_3 concentration at Wilmington, Wooster, and McConnelsville, Ohio, from June 14 to August 31, 1974.

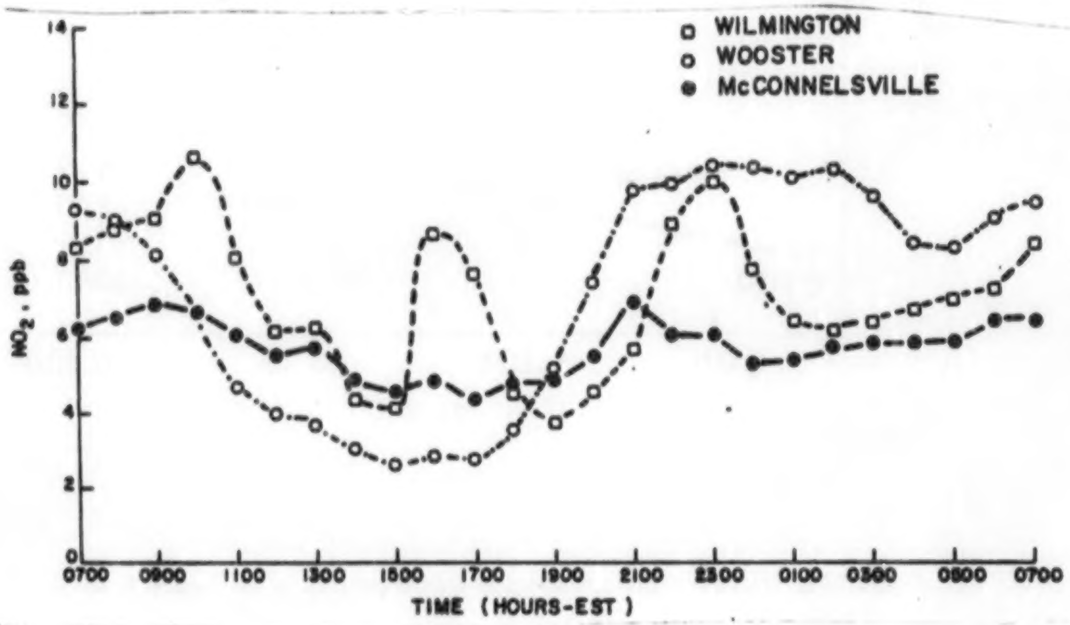

Figure 12-8. Mean diurnal NO_2 concentration at Wilmington, Wooster, and McConnelsville, Ohio, from June 14 to August 31, 1974.

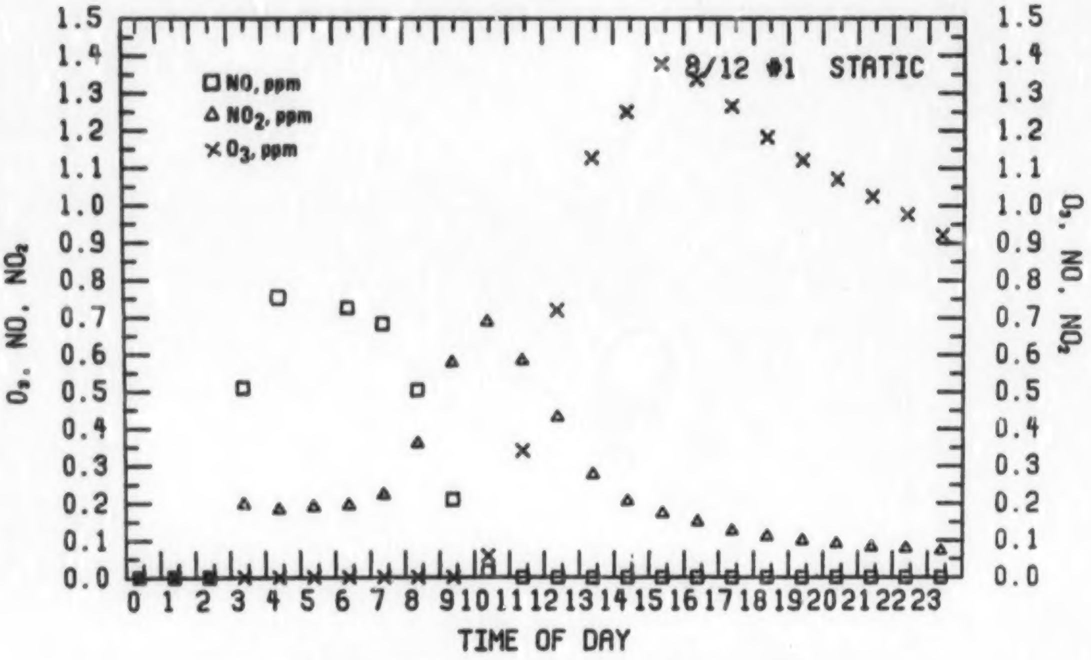

Figure 12-9. First day chamber concentration profiles.

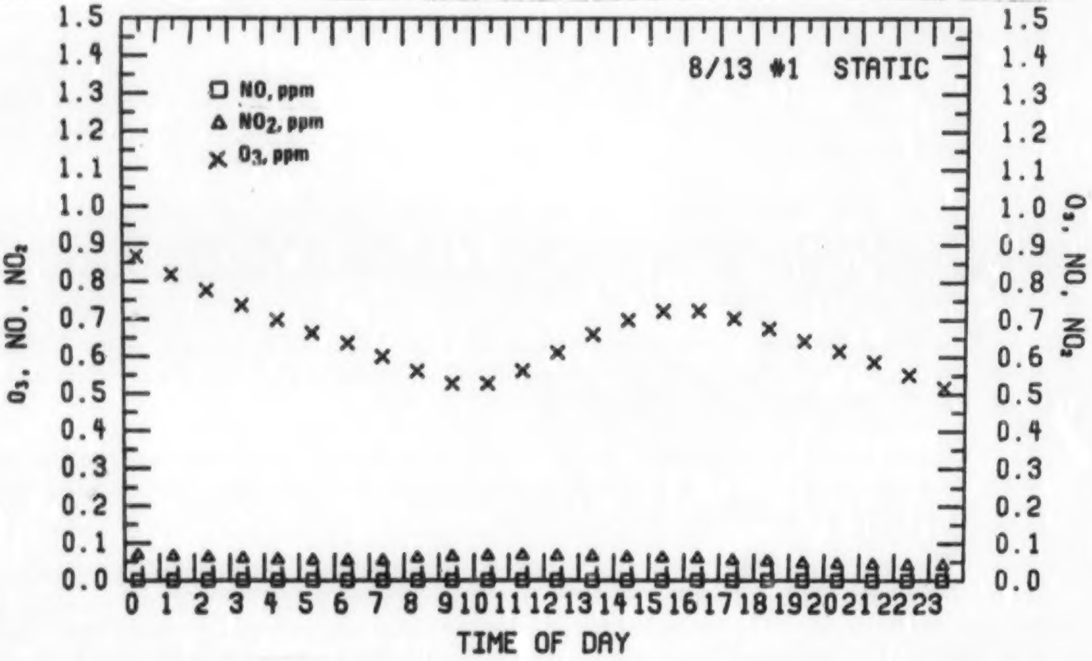

Figure 12-10. Second day chamber concentration profiles.

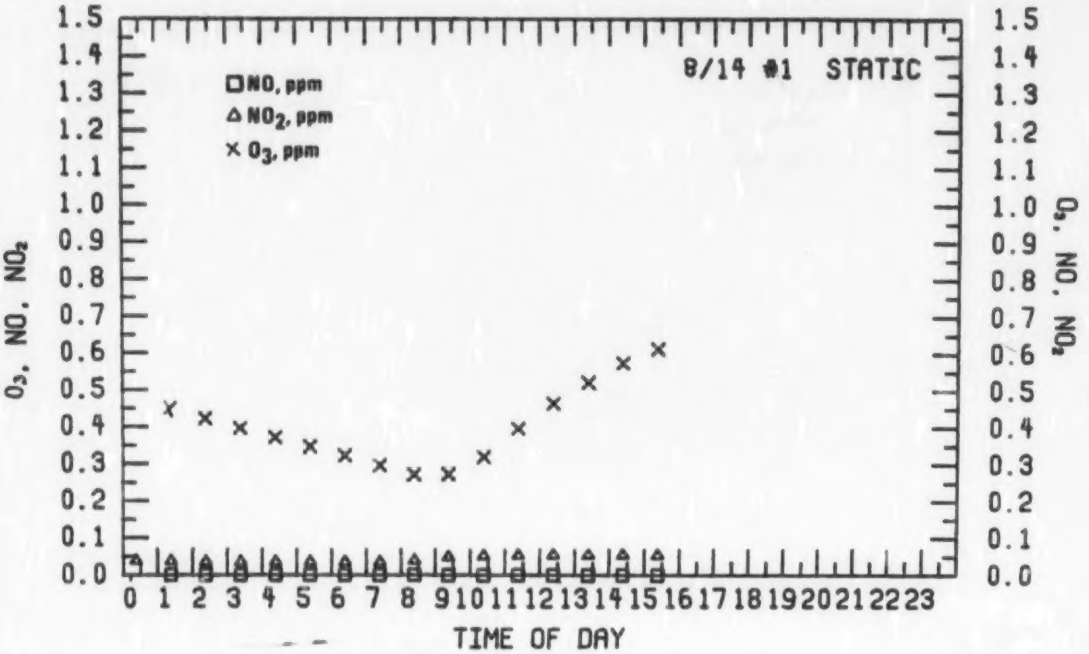

Figure 12-11. Third day chamber concentration profiles.

In Figure 12-12, the continuity of a 3-day run can better be seen. In this run, there was a 95 percent dilution of the system in 24 hours starting at the time of NO_x crossover. The NO_x became virtually undetectable, and the second and third day O_3 concentrations achieved values of approximately 0.25 ppm. The O_3 destructive side of these diurnal curves is less steep than in ambient air.

Table 12-4 is similar to Table 12-1. It reemphasizes the fact that in partially spent photochemical urban systems, O_3 can be generated in concentrations above the NAAQS with low concentrations (ppb) of NO_x and high NMHC/NO_x ratios.

The smog chamber data also suggest that the role of so-called "fossil" O_3 is to provide a high minimum to build a high maximum on the next day. The "fossil" O_3 unaugmented by subsequent synthesis probably cannot provide concentrations over the NAAQS for more than a day or two.

The smog chamber data indicate that the "dilution" effect (i.e., more efficient O_3 generation per molecule of NO_x with dilution) is an important process in delivering high O_3 concentrations to nonurban areas.

Smog chamber experiments have produced many of the characteristics of rural high O_3 atmospheres. With increasing experience of operation, better simulations will undoubtedly result.

At the Research Triangle Institute, it is felt that atmospheric chemical problems in general and the high rural O_3 problem in particular will yield to a three-faceted approach: field measurements, experimentation in smog chambers, and mathematical modeling. Each single facet has its limitations, but iterative studies using the combined approach should yield useful information and solutions to current problems of atmospheric chemistry.

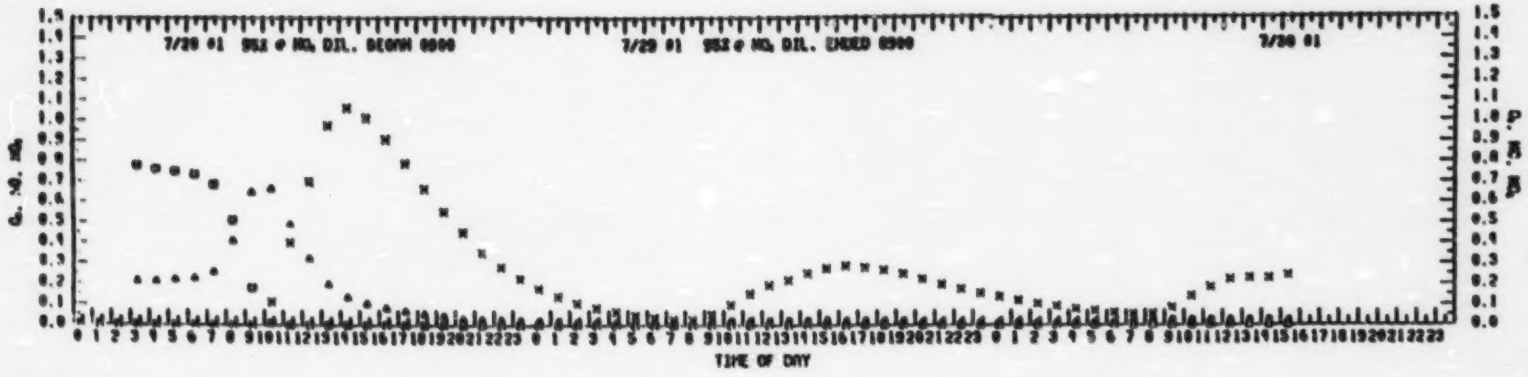

Figure 12-12. Typical 3-day profiles for NO (□), NO_2 (Δ), and 0_3 (x).

Table 12-4. SELECTED RESULTS FROM THE AUGUST 4-6 THREE-DAY RUNS

Chamber No. Date	Percent dilution, time of dilution initiation	Initial NMHC/NO$_x$ concentrations, ppmC/ppm	NMHC/NO$_x$ ratios	Maximum O$_3$ first day, ppm	Subsequent days	Precursors (ppm) at sunrise		NMHC/NO$_x$ ratios	Min. O$_3$, ppm	Max. O$_3$, ppm	Net O$_3$, ppm	Σ Solar rad. at O$_3$ max (Langley's)
						NO$_x$	NMHC					
Chamber No. 1	77% @ 0810	7.35 0.936	7.895	1.338	2	0.017	1.13	66.471	0.114	0.479	0.365	9.81
August 4-6					3	0.012	0.79	65.833	0.174	0.293	0.119	5.64
Chamber No. 2	0820	4.41 0.232	19.009	0.806	2	0.009	0.88	97.778	0.054	0.366	0.312	9.72
August 4-6					3	0.006	0.62	103.333	0.128	0.233	0.105	5.64
Chamber No. 3	0830	4.40 0.679	6.480	0.956	2	0.010	0.74	74.000	0.094	0.350	0.256	9.25
August 4-6					3	0.007	0.58	82.857	0.114	0.238	0.124	5.64
Chamber No. 4	0805	1.09 0.107	10.187	0.488	2	0.001	0.61	610.000	0.041	0.214	0.173	9.67
August 4-6					3	0.004	0.47	117.500	0.056	0.179	0.123	5.64

13. OZONE TRANSPORTED TO NANTUCKET, MA
OCTOBER 1975

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Plants of Bel-W3 tobacco, a plant easily injured by ozone, were used in conjunction with Mast oxidant meters to confirm that oxidants occurring on Nantucket during the summer of 1975 were from a distant source. The oxidant, probably ozone, was maximal on southwest winds with very little ozone transported to Nantucket Island on east and northeast winds. Since Nantucket has no means of producing the high levels of ozone indicated by the Mast meters and plants that were positioned across the island, a likely source may be the urban areas about 200 or more miles over ocean to the southwest.

Ozone flecking of Bel-W3 tobacco has been shown to have a direct correlation with hours of ozone higher than 0.04 ppm if a sufficient number of plants are used in a grid system. Using Nantucket Island as a single grid with nine areas of tobacco plants across it, the direct correlation with daylight hours of ozone was confirmed. Nantucket experienced 260 daylight hours (6 a.m. to 9 p.m.) with ozone concentrations ≥ 0.04 ppm and 351 hours of night-time ozone (10 p.m. to 5 a.m.) ≥ 0.04 ppm. All ozone levels above 0.06 ppm between June 3 and August 12, 1975, occurred when the winds were from the southwest.

INTRODUCTION

Oxidant injury to plants has been well documented, especially for urban areas.[1,2] The major constituent of high oxidant levels in the atmosphere is probably ozone, which was commonly thought to be relatively labile.[3,4]

Bel-W3 tobacco plants are widely used as indicators of ozone pollution, but several previous studies report that the relationship between oxidant doses and injury to tobacco leaves is nonlinear.[5,6] A grid layout of tobacco plants has been used in previous work, which showed that leaf damage and hours of ozone greater than 0.04 ppm were linearly related, if a sufficient number of tobacco plants are distributed in a grid formation over an area at least 0.5 mile in diameter. The grid system seems to eliminate the large deviations observed between individual plant responses to ozone.[7]

The study reported here was conducted on Nantucket Island, MA, an island 30 miles to the southeast of Woods Hole, MA, and about 200 miles to the northeast of the Middle Atlantic States. The objectives of the study were: (1) to demonstrate long-range transport of ozone, and (2) to evaluate tobacco injury due to ozone using a grid layout. This was the first large-scale field test of that system.

MATERIALS AND METHODS

Seeds of the Bel-W3, ozone-sensitive, tobacco were grown in a charcoal filtered air chamber for a period of 6 weeks. The plants were then transplanted into uniform, steamed soil at nine areas on Nantucket Island on June 5, 1975. The areas each consisted of three points containing at least three plants at each point. The tobacco plants were observed from June 5 to August 11, 1975. All plants were shaded (approximately 50 percent), watered, and fertilized. The injury due to ozone on each leaf was scored weekly by inspection of area flecked.

Ozone was monitored with a calibrated Mast oxidant meter fitted with strip chart recorders, and hourly maximums were recorded. Mast devices were placed on the opposite ends of Nantucket. The ozone levels were correlated to wind direction, which was monitored on a standard anemometer positioned approximately 40 feet above sea level at Quaise (middle-north location on the Island).

The mean and standard deviation of percent leaf injury for all nine areas of the grid were related to the number of daylight hours (6 a.m. to 9 p.m.) during which the maximum ozone level equaled or exceeded 0.04 ppm.

RESULTS

The wind rose of Figure 13-1 points out the predominance of southwest winds during the study period. The figure also relates wind direction to the cumulative hours of ozone $\geq$ 0.04 ppm. The ozone transport on southwest winds is clearly seen when compared to the lack of ozone transported to the island from the east. Table 13-1 indicates that the cumulative hours of ozone $\geq$ 0.04 ppm were more frequent at night (10 p.m. to 5 a.m., with 351 hours) than during the day (6 a.m. to 9 p.m., with 260 hours). The total for the study period was 611 hours. The highest single hourly ozone level was 0.205 ppm, with levels over 0.08 ppm common on southwest winds.

Table 13-2 relates increasing plant injury at individual areas to increasing cumulative daylight hours of ozone $\geq$ 0.04 ppm. The linearity of the data in Table 13-2 is illustrated in Figure 13-2.

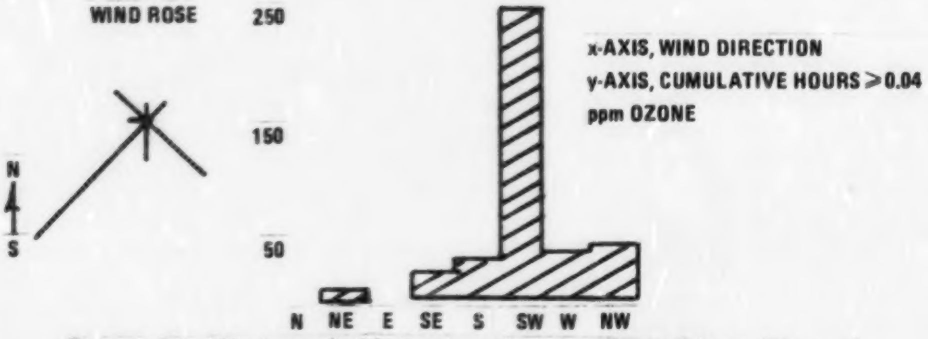

Figure 13-1. Wind rose (left) showing wind directions of June, July, and August 1975. Cumulative hours of ozone related to wind direction (right) shows the predominance of ozone transported to Nantucket Island, MA, from the southwest.

Table 13-1. CUMULATIVE HOURS DURING WHICH OZONE LEVELS WERE $\geq$ 0.04 ppm

	Σ hours
Daylight hours (6 a.m. to 9 p.m.) of ozone	260
Night hours (10 p.m. to 5 a.m.) of ozone	351
Total hours of ozone	611

DISCUSSION

The appropriately calibrated Mast oxidant meters confirmed that there were no detectable sources of ozone pollution on Nantucket Island itself. The two Mast meters and the nine-area tobacco plant grid did indicate the presence of frequently occurring high concentrations of ozone. The linearity of the plant injury due to ozone was based on daylight hours of ozone, since plants seemed to be susceptible to injury from ozone only when the stomata were open.[2] The linear relationship between plant injury and hours of ozone $\geq$ 0.04 ppm developed by the use of the grid system[7] appears to be reproducible. The slopes of these relationships do vary, but not significantly, and at this time no concrete explanation for this variation can be given.

The evidence for the presence of ozone on Nantucket, when related to the recorded wind directions, suggests that a likely source for the majority of ozone was the urban areas about 200 miles or more to the southwest of Nantucket. Furthermore, since

Table 13-2. CUMULATIVE DAYLIGHT HOURS (6 a.m. to 9 p.m.) OF OZONE $\geq$ 0.04 ppm, AND MEAN PERCENT PLANT INJURY DUE TO OZONE AT EACH AREA OF THE GRID

Date	Hours of ozone $\geq$ 0.04	Mean percent plant injuries at nine areas[a]								
		I	II	III	IV	V	VI	VII	VIII	IX
5/9/75	27	1	0	2	0	0	2	3	0	4
5/16/75	55	5	2	11	3	1	8	9	3	11
5/23/75	72	6	12	14	15	12	12	10	4	12
5/30/75	79	9	14	18	21	13	18	16	5	14
6/11/75	140	25	32	40	39	39	28	31	25	26
6/22/75	154	22	41	38	43	40	31	39	27	32
6/30/75	208	39	48	59	56	55	34	37	38	30
7/6/75	250	52	52	62	66	55	40	52	42	53
7/11/75	260	52	51	73	59	54	54	48	50	48

[a] Mean percent injury for nine plants per area. Area names and locations:

I. U.S.C.G. Loran Station (SE)
II. Shimo (middle, N)
III. Ram Pasture (SW)
IV. Squam (NE)
V. Mile Stone Road (middle)
VI. Bartlett Farm (SSW)
VII. Univ. of Mass., Quaise (N)
VIII. M.S.P.C.A. Reserve (NW)
IX. Nantucket Cranberry Co. (middle, E)

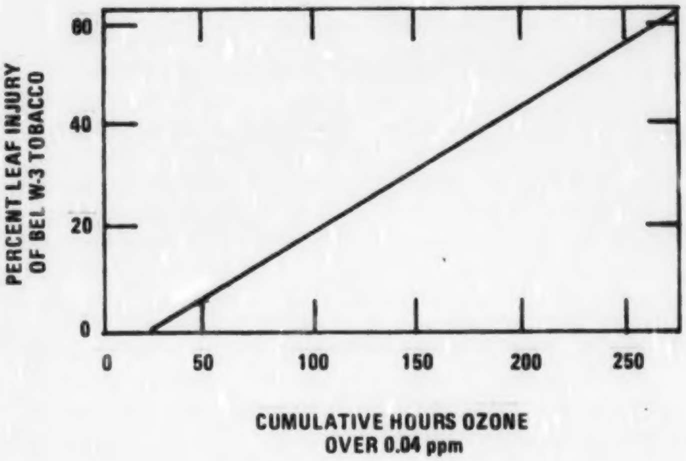

Figure 13-2. Percent leaf injury of Bel-W3 relates linearly to the daylight hours of ozone ≥ 0.04 ppm.

ozone is produced by a photoreaction of hydrocarbons and nitrogen oxides, the common night-time occurrence of ozone supports the contention that ozone is produced in the light and later transported to the island by wind. The long range transport of ozone might be considered in relation to the surface over which the ozone is being transported. This study confirms that ozone is capable of long range transport over the ocean surface, but the range of ozone transport may be quite different over a forest or a mountain range.

Communities and others interested in local air quality, but unable to afford the cost of buying and maintaining monitoring equipment, might be able to utilize a grid system of tobacco plants for a semi-quantitative estimate of daylight hours of ozone. A proper set of standard curves should be developed for this purpose. The concept of using plants as air quality monitors may even have advantages over a single purpose monitoring device. A plant is capable of integrating many subtle variations in any given microenvironment and, therefore, is measuring the true quality of its environment rather than a single aspect or substance in that environment.

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